

Anno 2010-2011 **FISICA MODERNA - ELENCO FOTOCOPIE**
TESTI

BARROW “Chimica fisica”

Cap. 2 - teoria cinetica

ENGE-WEHR-RICHARDS “Introduction to Atomic Physics”

Cap. 1 - the atomic view of matter

Cap. 2 - the atomic view of electricity

Cap. 3 - the atomic view of radiation

Cap. 4 - the atomic models of Rutherford and Bohr

Cap. 5 - waves and particles

DEKKER – “Solid State Physics”

Cap. 2 – the specific heat of solids and lattice vibrations

RICHTMYER-KENNARD-COOPER “Modern Physics”

Cap. 5 - the origin of quantum theory

Cap. 7 - X-rays

EISBERG-RESNICK “Quantum Physics”

Cap. 4 – Bohr’s model of the atom

ALONSO – FINN “III-Quantum and statistical physics”

Cap. 3 – atoms with one electron (solo cenni, vedere quanto fatto sugli appunti)

Cap. 10 - classical statistical mechanics

Cap. 12 - thermal properties of gases

questo considerando la sezione orizzontale della curva critica di Fig. 1.10.

- 30 Supponete che venga concordato che il punto di congelamento normale dell'acqua abbia una temperatura di 100 in una scala assoluta. Quale sarebbe allora la temperatura normale di ebollizione dell'acqua?
- 31 Un tubo con una parete porosa consente a 0,53 litri di azoto di fuoriuscire in un minuto da una pressione di 1 atm in una camera a vuoto spinto. Quale sarebbe la quantità di gas uscente nelle medesime condizioni trattandosi di elio, o vapori di CCl_4 e UF_6 ?
- 32 Nel 1846 Graham riportò i dati seguenti per il tempo di effusione di vari gas rispetto all'aria:

gas	aria	O_2	CO	CH_4	CO_2
tempo	1,000	1,053	0,987	0,765	1,218

In che misura questi dati si accordano alla legge effusimetrica di Graham?

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Capitolo 2 BARROW

Teoria cinetica-molecolare dei gas

2.1. Modello cinetico-molecolare dei gas

Nel Capitolo 1 lo studio del comportamento fisico dei gas è stato affrontato dal punto di vista empirico senza preoccuparsi di rispondere a semplici domande del tipo: perché un gas segue la legge di Boyle? Perché obbedisce alla legge di Gay Lussac? Perché possiede una certa viscosità? E così via. In questo capitolo si cercherà, invece, di approfondire la natura dei gas, e diventerà facile rispondere a domande simili.

La teoria cinetica-molecolare, comunque, non viene introdotta soltanto per fornire una spiegazione delle leggi dei gas; il motivo principale per cui è stata sviluppata è di mettere in evidenza, di definire, gli aspetti quantitativi del mondo molecolare.

La natura dei gas non è direttamente deducibile dalle proprietà che vengono misurate. È necessario servirsi di questi dati in modo indiretto. Di norma, si procede formulando delle ipotesi sulle caratteristiche intrinseche dei gas e poi sulle basi di queste, si deducono le proprietà fisiche.

La validità delle ipotesi fatte viene verificata confrontando le proprietà dedotte e quelle misurate. Un insieme di definizioni di caratteristiche intrinseche dei gas costituisce un cosiddetto *modello*.

Le leggi e le proprietà dei gas descritte nel Capitolo 1 possono essere studiate adottando come modello, ad esempio, un gas costituito da un grande numero di piccole particelle, chiamate *molecole*, che si muovono caoticamente urtandosi fra loro e urtando le pareti del recipiente. Non è il caso di riportare qui le nozioni chimiche che stanno alla base del concetto di molecole. Sarà sufficiente ricordare che l'idea che un composto chimico fosse costituito da atomi ha subito una lenta evoluzione ed è stata universalmente accettata soltanto nel 1800, insieme ai concetti di atomo e molecola. L'applicazione della teoria atomistica in campo chimico si è dimostrata molto valida per spiegare la composizione e la trasformazione di sostanze chimiche; non ha fornito, invece informazioni sulla misura, la forma e le proprietà delle singole molecole.

La sola acquisizione del concetto di molecola, tuttavia, è servita da base per lo studio del comportamento dei gas; mediante l'applicazione della cosiddetta *teoria cinetica-molecolare dei gas* si sono raccolte numerose informazioni circa le proprietà delle singole molecole. Boltzmann, Maxwell e Clausius nel tardo '800, diedero con il loro lavoro, il massimo contributo allo sviluppo di questa teoria.

Mediante la teoria cinetica-molecolare verranno desunte, in questo capitolo, alcune proprietà dei gas. In taluni casi la teoria verrà esposta in forma semplificata, per non appesantirne le caratteristiche con operazioni matematiche troppo complesse. In un secondo tempo, verranno approfondite alcune parti semplificate di tale teoria per completare l'analisi dettagliata del moto delle molecole in un gas.

Il modello cinetico-molecolare di un gas può essere espresso postulando le seguenti condizioni:

- 1) Un gas è costituito da un grande numero di particelle o molecole assai piccole rispetto alla loro distanza e alle dimensioni del recipiente.
- 2) Le molecole sono soggette ad un movimento caotico continuo, assolutamente casuale.
- 3) Gli urti fra le molecole e contro le pareti del recipiente sono perfettamente elastici e all'atto della collisione non vi è alcuna perdita di energia traslazionale per conversione in energia interna.

La prima cosa da fare, utilizzando questo modello, è di stabilire se esso consenta o meno di ricavare le proprietà osservabili nei gas.

In base al modello cinetico-molecolare è possibile calcolare la pressione esercitata da N molecole di massa m contenute in un recipiente cubico di lato l . Gli urti delle molecole contro le pareti del recipiente sono responsabili della pressione che il gas esercita verso l'esterno. Per mantenere, quindi, un volume costante in equilibrio si dovrà opporre una pressione uguale, ma opposta, diretta verso l'interno, che potrà essere, ad esempio, semplicemente la resistenza offerta dalle pareti del recipiente.

Consideriamo, per cominciare, una sola delle N molecole. Indichiamo la sua velocità e direzione con \mathbf{u} , scritto in grassetto per contraddistinguere una grandezza vettoriale. Il simbolo u indicherà, invece, la velocità scalare. Il vettore \mathbf{u} può essere decomposto nelle sue componenti u_x , u_y e u_z che sono perpendicolari alle pareti del recipiente come si vede in Fig. 2.1. (Notate che u_x , ad esempio, ci dà informazioni sulla direzione potendo essere positivo o negativo. Questo comporta un moto positivo o negativo nella direzione delle x . D'altra parte u_x che è lo scalare del vettore \mathbf{u}_x può assumere solo valori positivi).

Consideriamo ora, l'effetto della componente di velocità, lungo l'asse delle x , su di una molecola. Come risultato di tale effetto, la molecola urterà prima una delle pareti del recipiente, perpendicolare all'asse delle x , e dopo aver rimbalzato urterà, di conseguenza, la parete opposta. L'insieme di questi urti, secondo la teoria cinetica-molecolare produce la pressione dei gas.

La forza esercitata dall'urto di una molecola sulla parete di un recipiente si può calcolare utilizzando la seconda legge del moto di Newton. Questa legge afferma che la velocità con cui cambia la quantità di moto di una particella, che si muove in una certa direzione, è uguale alla forza agente sulla particella, nella stessa direzione. La quantità di moto con cui la particella si avvicina alla parete A di Fig. 2.1. è mu_x . Dopo l'urto la molecola si muove di nuovo con u_y e u_z immutati, ma con un valore di u_x , e quindi anche di mu_x , di segno opposto, come risulta evidente dalla Fig. 2.2. Così la parete oppone all'impatto una forza che determina un cambiamento della quantità di moto pari a $2mu_x$ in direzione perpendicolare alla parete.

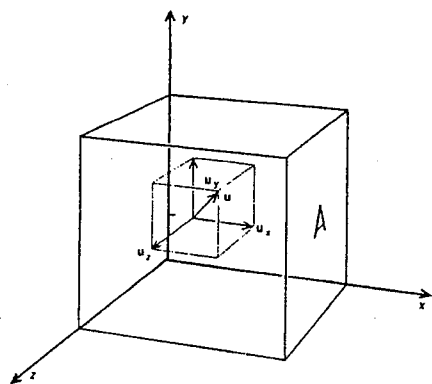


Figura 2.1.
Rappresentazione delle coordinate della velocità molecolare e delle componenti della velocità impiegate per la derivazione della pressione del gas.

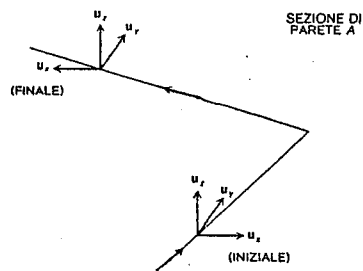


Figura 2.2.
L'inverso di u_x come risultato di una collisione con la parete A .

numero di urti per secondo che si verificano sulla stessa parete. Poiché le molecole percorrono in 1 s una distanza pari a u_x , e poiché la distanza percorsa fra una collisione e la successiva sulla parete A è $2l$, il numero degli urti per secondo su A è $u_x/2l$. La velocità con cui cambia il momento, cioè la variazione di momento per secondo è perciò:

$$2mu_x \frac{u_x}{2l} = F_x \quad [1]$$

Questa è la forza che la parete A oppone all'urto di una molecola. Poiché la forza per unità di area rappresenta la pressione, la pressione relativa alla parete A è data da:

$$P_x = \frac{F_x}{l^2} = \frac{2mu_x(u_x/2)}{l^3} = \frac{2mu_x(u_x/2)}{V} \quad [2]$$

dove $V = l^3$ è il volume del recipiente. Si può ora ammettere che la pressione sia identica per tutte le pareti e agisca su queste perpendicolarmente. Possiamo così fare a meno delle restrizioni legate alla parete A e a specifiche direzioni, eliminando la notazione vettoriale. Avremo pertanto:

$$P = \frac{mu_x^2}{V} \quad [3]$$

Consideriamo ora, invece, che nel recipiente cubico vi siano N molecole. Secondo il nostro modello queste molecole agiscono l'una indipendentemente dall'altra portando ciascuna un contributo alla pressione secondo un termine simile all'Eq. [3]. (Se esse però interagiscono, dando luogo a urti occasionali fra loro, il fatto che la quantità di moto, nella sua componente direzionale, debba essere conservato, comporta un risultato identico a quello che si avrebbe se le particelle fossero completamente indipendenti). La somma dei contributi di pressione delle N molecole si può indicare come:

$$P = \sum_i \frac{(mu_x^2)_i}{V} \quad [4]$$

Possiamo considerare il caso in cui tutte le molecole abbiano la stessa massa. Il modello da noi assunto prevede che le molecole si muovano in tutte le direzioni con velocità diverse e così u_x e u_x^2 saranno diversi per ciascuna molecola.

Se si indica il valor medio di u_x^2 per le N molecole di gas con $\overline{u_x^2}$ — si può sviluppare l'Eq. [4], allo scopo di definire la pressione per mantenere N molecole di gas confinate entro il volume V , nel modo seguente:

$$P = \frac{m}{V} \sum_i (u_x^2)_i = \frac{m}{V} N \overline{u_x^2} = \frac{Nm \overline{u_x^2}}{V} \quad [5]$$

Una relazione fra la pressione, dovuta alle N molecole, e la velocità media delle molecole è, comunque, più conveniente.

La relazione fra il quadrato delle componenti della velocità, precedentemente vista, e il quadrato della velocità medesima è espressa dalla seguente relazione:

$$u^2 = u_x^2 + u_y^2 + u_z^2 \quad [6]$$

Per un grande numero di molecole che si muovono in ogni direzione in modo del tutto casuale:

$$\overline{u_x^2} = \overline{u_y^2} = \overline{u_z^2} \quad [7]$$

e perciò:

$$\overline{u^2} = 3\overline{u_x^2} \quad [8]$$

(Si noti che u^2 e $\overline{u^2}$ sono delle grandezze scalari, cioè non vettoriali, che non indicano, pertanto, la direzione delle velocità molecolari, ma solo il loro modulo). La sostituzione dell'Eq. [8] nell'Eq. [5] dà la relazione desiderata fra P e $\overline{u^2}$; cioè

$$P = \frac{1/3 N m \overline{u^2}}{V} \quad \text{oppure} \quad PV = \frac{1}{3} N m \overline{u^2} \quad [9]$$

Questa importante equazione rappresenta esattamente quanto volevamo ottenere, cioè spiegare il significato della pressione di un gas sulla base dei postulati del modello cinetico-molecolare del paragrafo 2.1.

Questa relazione, per ora, non può essere confrontata con le leggi empiriche dei gas, ma nel prossimo paragrafo verranno esposte delle altre considerazioni che consentiranno un confronto del genere.

2.3. Energia cinetica e temperatura

Spesso, come nel presente caso, è più conveniente impiegare l'energia cinetica invece della velocità delle molecole. L'energia cinetica media di una molecola di un gas viene indicata con \overline{ke} . Questa grandezza è legata al quadrato della velocità molecolare dell'espressione:

$$\overline{ke} = \frac{1}{2} m \overline{u^2} \quad [10]$$

L'equazione [9] può allora essere sviluppata dopo averla posta nella forma:

$$PV = \frac{2}{3} N \left(\frac{1}{2} m \overline{u^2} \right)$$

in:

$$PV = \frac{2}{3} N \overline{ke} \quad [11]$$

Le relazioni empiriche del Capitolo 1 si riferivano a quantità molari di gas. Le relazioni presenti, invece, si riferiscono, come ad esempio, nel caso \overline{ke} , alle singole molecole. Per considerare un insieme di molecole è necessario ricorrere al numero di Avogadro \mathcal{N} che è il numero di molecole contenute in una mole, se N è il numero di molecole, e n quello delle moli varrà:

$$N = n \mathcal{N} \quad [12]$$

L'equazione [11] può ora essere scritta:

$$PV = \frac{2}{3} n (\mathcal{N} \overline{ke}) \quad [13]$$

Se introduciamo, inoltre, il termine KE per indicare l'energia cinetica di un numero di molecole pari a quello di Avogadro, si può riscrivere l'Eq. [11] nel modo seguente:

$$PV = \frac{2}{3} n KE \quad [14]$$

A questo punto è bene ricordare l'espressione empirica:

$$PV = nRT$$

e confrontare questa espressione con l'Eq. [14] ricavata mediante la teoria cinetica-molecolare. La discrepanza apparente fra le due relazioni non presentò alcun problema neppure dal punto di vista storico. Calore e temperatura, infatti, furono spesso associate, sia pure qualitativamente, all'idea di agitazione e moto delle particelle in un materiale caldo. Era perciò giustificato far collimare l'espressione teorica con la legge sperimentale ponendo $\frac{2}{3} KE$ uguale a RT , o:

$$KE = \frac{3}{2} RT \quad [15]$$

Pertanto se l'energia traslazionale di un numero di molecole pari al numero di Avogadro, cioè di 1 mole di gas, ha il valore di $\frac{3}{2} RT$, allora la legge dei gas, riassunta nella $PV = nRT$ si può dedurre anche dai postulati della teoria cinetica-molecolare.

Verranno ora ricavate alcune delle relazioni empiriche del Capitolo 1. L'espressione $PV = \frac{2}{3} n KE$, insieme con il postulato $KE = \frac{3}{2} RT$, permettono di ricavare, ad esempio, la legge di Boyle e quella di Gay Lussac. Inoltre, a patto che i postulati della teoria cinetica-

molecolare e da ogni altra proprietà caratteristica delle molecole. Questa espressione, $\overline{u^2} = \frac{3RT}{m}$, può valere per due gas diversi, alla stessa temperatura e pressione, soltanto se volumi uguali di questi gas contengono lo stesso numero di moli o molecole. Viene così dedotta e confermata l'ipotesi di Avogadro.

La legge di Dalton, inoltre, è una conseguenza diretta dei postulati originali poiché in questi si affermava che le molecole non interagiscono e occupano un volume trascurabile. In tale caso le molecole di un certo tipo di gas non avranno alcun effetto su quelle di un altro gas. Per una miscela di gas, pertanto, secondo la teoria cinetica-molecolare, la pressione totale P deve essere la somma delle pressioni di ciascun componente, cioè:

$$P = P_1 + P_2 \dots$$

2.4. Valori numerici per le energie e per le velocità molecolari

In questo paragrafo si cercherà di definire alcune proprietà delle molecole che costituiscono un gas, in particolare la velocità e l'energia. È stato già messo in evidenza che i postulati qualitativi della teoria cinetica molecolare descrivono in modo sufficientemente accurato il mondo molecolare e consentono di ricavare le leggi dei gas ideali.

Una informazione quantitativa, invece, deriva dal fatto che l'energia cinetica di un numero di molecole pari al numero di Avogadro deve essere $\frac{3}{2} RT$.

Il valore di R , dato nel paragrafo 1.4., pari a $8,3143 \text{ J grado}^{-1} \text{ mole}^{-1}$ permette poi di ricavare il contributo d'energia per il moto traslazionale di 1 mole di un qualsiasi gas ideale a 25°C :

$$\frac{3}{2} RT = \frac{3}{2} (8,31) (298) = 2480 \text{ J mole}^{-1}$$

Si può, quindi, calcolare l'energia cinetica media di una molecola di gas come:

$$\overline{ke} = \frac{KE}{\mathcal{N}} = \frac{3}{2} \frac{R}{\mathcal{N}} T \quad [16]$$

Poiché buona parte della nostra successiva esposizione riguarda le energie dei singoli atomi e molecole, è utile introdurre una nuova costante chiamata costante di Boltzmann, così definita:

$$k = \frac{R}{\mathcal{N}} = 1,3806 \times 10^{-23} \text{ J grado}^{-1} \quad [17]$$

La costante di Boltzmann si può allora considerare, la costante dei gas riferita alle singole molecole, mentre l'energia cinetica media per molecola, si può indicare con:

$$\overline{ke} = \frac{3}{2} kT \quad [18]$$

che a 25°C ha un valore numerico pari a:

$$\overline{ke} = \frac{3}{2} (1,380 \times 10^{-23}) (298) = 4,11 \times 10^{-21} \text{ J}$$

È difficile allo stato attuale apprezzare quale importanza abbiano questi valori dell'energia cinetica; ciò diventerà più chiaro in seguito. È opportuno quindi, per ora, riferirsi a delle proprietà molecolari di più immediata comprensione, ad esempio, la velocità con cui le molecole si muovono.

L'energia cinetica di un numero di molecole pari al numero di Avogadro si può scrivere:

$$KE = \mathcal{N} \left(\frac{1}{2} m \overline{u^2} \right) = \frac{1}{2} M \overline{u^2} \quad [19]$$

dove M è la massa molare. Combinando questa relazione con quella relativa al postulato

colare $u^2 = 3 RT/M$ oppure:

$$\sqrt{u^2} = \sqrt{\frac{3RT}{M}} \quad [20]$$

Il termine $\sqrt{u^2}$, dal significato non facilmente intuibile, rappresenta la radice quadrata della velocità quadratica media, la sua determinazione implica che tutte le velocità molecolari vengano elevate al quadrato, che se ne faccia la media e infine si valuti la radice quadrata del valor medio. Ciò consente di ottenere una grandezza che è diversa da una semplice velocità media. La differenza da essa, tuttavia, come vedremo nel paragrafo 2.6., è limitata a circa il 10%. Per ora, i valori di $\sqrt{u^2}$ verranno considerati come se indicassero delle velocità molecolari medie.

Nel caso di N_2 a 25 °C, per esempio, M ha in unità SI, il valore 0,02802 kg e quindi avremo:

$$\begin{aligned} \sqrt{u^2} &= \sqrt{\frac{3(8,3143)(298,15)}{0,02802}} \\ &= 515 \text{ m s}^{-1} \\ &= 1150 \text{ mph} \end{aligned} \quad [21]$$

La Tab. 2.1. riporta i dati relativi ad altre semplici molecole.

Poiché l'energia cinetica, a una certa temperatura, è la stessa per tutte le molecole, indipendentemente dalla massa, le molecole leggere avranno velocità più grandi delle molecole pesanti. Si può notare inoltre, che come per le velocità molecolari, che possono essere definite mediante le loro componenti nelle tre direzioni perpendicolari, cioè: $u^2 = u_x^2 + u_y^2 + u_z^2$ un uguale procedimento può essere applicato al valor medio delle energie cinetiche medie:

$$\frac{1}{2} m \overline{u^2} = \frac{1}{2} m \overline{u_x^2} + \frac{1}{2} m \overline{u_y^2} + \frac{1}{2} m \overline{u_z^2}$$

oppure

$$\overline{ke} = (\overline{ke})_x + (\overline{ke})_y + (\overline{ke})_z \quad [22]$$

Poiché l'energia di queste componenti medie è uguale, e vale $\overline{ke} = 3/2 kT$ ne segue:

$$(\overline{ke})_x = (\overline{ke})_y = (\overline{ke})_z = \frac{1}{2} kT \quad [23]$$

Le tre direzioni perpendicolari in cui sono state scomposte le velocità e le energie vengono chiamate *gradi di libertà*. Possiamo così affermare che l'energia traslazionale media di una molecola per grado di libertà è $1/2 kT$. Vedrete in seguito come questa affermazione sia largamente applicabile e sia una guida importante nello studio delle energie molecolari.

Tabella 2.1. Velocità medie di molecole di gas [uguale a $0,921 \sqrt{u^2}$ a 25 °C (298 K) e 1000 °C (1273 K)].

Gas	25 °C		1000 °C	
	m s ⁻¹	mph (*)	m s ⁻¹	mph (*)
H ₂	1770	3960	3660	8180
He	1260	2820	2600	5830
H ₂ O	590	1320	1220	2730
N ₂	470	1060	970	2190
O ₂	440	990	910	2050
CO ₂	380	840	780	1740
Cl ₂	300	670	620	1380
HI	220	490	450	1010
Hg	180	400	370	830

(*) Un miglio equivale a 1609,3 m.

2.5. Distribuzione di velocità molecolari lungo una dimensione

Avendo considerato e tabulato alcune velocità medie molecolari è ora opportuno investigare più a fondo sui valori specifici delle velocità molecolari da cui derivano i valori medi già trovati.

La *distribuzione di Boltzmann* è la relazione fondamentale per trattare questioni relative al numero di molecole che abbiano velocità ed energie diverse. La deduzione di questa importante relazione viene differita a dopo aver studiato le regole quantiche, che come si vedrà, dominano il comportamento molecolare. Qui se ne anticiperanno i risultati finali, ricavati invece estesamente nel Capitolo 5, e la distribuzione di Boltzmann verrà impiegata per ottenere le informazioni desiderate sulle distribuzioni delle velocità molecolari.

Secondo il modello su cui è basata la teoria cinetica-molecolare, le molecole di un gas si muovono caoticamente con diverse velocità e direzioni. Queste velocità possono essere riportate su un diagramma simile a quello di Fig. 2.3. dove ciascun punto rappresenta, con la sua distanza dall'origine, l'intensità della velocità e con il verso, rispetto all'origine, la direzione in cui si muove la particella. L'indicazione con una freccia, del vettore velocità, anche se non è in sostanza indispensabile, rende più chiaro il diagramma.

Poiché i gas si comportano nello stesso modo in ogni direzione e sono quindi *isotropi*, un diagramma come quello della Fig. 2.3., per un numero sufficientemente grande di molecole, deve essere lo stesso in tutte le direzioni. La natura delle variazioni della densità dei punti di velocità, che escono dall'origine, è dovuta alla distribuzione delle velocità molecolari e sarà studiata in questo paragrafo e nel paragrafo 2.6.

In questo paragrafo studieremo in particolare la distribuzione delle velocità molecolari lungo una direzione, ad esempio la direzione delle x . Secondo la Fig. 2.4., per fare questo è necessario trovare il rapporto fra il numero dei punti dN che si trovano negli elementi di volume, rappresentati in Fig. 2.4., e il numero totale di punti di velocità N . Dobbiamo, cioè, trovare la frazione dN/N dei punti di velocità, nell'intervallo di velocità compreso fra u_x e $u_x + du_x$. Secondo l'espressione della distribuzione di Boltzmann, questa frazione è

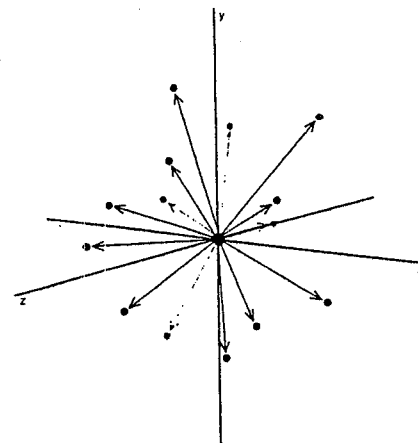


Figura 2.3.
Le velocità delle molecole. Ciascuna intensità e direzione è rappresentata dalla lunghezza e direzione delle frecce.

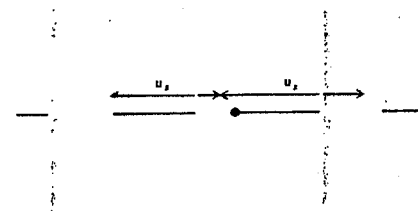


Figura 2.4.
I due elementi di volume che insieme contengono tutte le molecole che si muovono con velocità fra u_x e $u_x + du_x$.

26. proporzionale a un termine esponenziale il cui esponente esprime il rapporto fra l'energia cinetica corrispondente $1/2 mu_x^2$ e kT . Più esplicitamente:

$$\frac{dN}{N} = A e^{-(1/2) mu_x^2 / kT} du_x \quad [24]$$

dove A è una costante di proporzionalità. Questa costante può essere determinata tenendo presente che l'integrazione del membro a destra dell'Eq. [24], estesa a tutti i possibili valori di u_x fra 0 e ∞ , comprende tutti i punti descriventi la velocità. Così potremo scrivere:

$$\int_0^\infty A e^{-(1/2) mu_x^2 / kT} du_x = 1 \quad [25]$$

per cui la costante di proporzionalità risulta:

$$A = \frac{1}{\int_0^\infty e^{-(1/2) mu_x^2 / kT} du_x} \quad [26]$$

Il valore dell'integrale come si può vedere dall'Appendice 1 è $1/2 \sqrt{\pi}$, otterremo allora:

$$A = \sqrt{\frac{2m}{\pi kT}} \quad [27]$$

Infine si può scrivere l'equazione di distribuzione delle velocità lungo una direzione, per un campione di N molecole, nel seguente modo:

$$\frac{dN}{N} = \sqrt{\frac{2m}{\pi kT}} e^{-(1/2) mu_x^2 / kT} du_x \quad [28]$$

Grafici di questa funzione di distribuzione unidimensionale per l'azoto, a due diverse temperature, sono mostrati nella Fig. 2.5. a.

In Fig. 2.5., oltre alle velocità molecolari vengono riportate in ascissa le energie cinetiche. Si può verificare facilmente che l'energia cinetica totale per questo moto unidimensionale è in realtà $1/2 RT$ mole⁻¹. Questo si può già dedurre qualitativamente dalla figura, mentre una verifica più accurata può essere condotta costruendo un diagramma che abbia una scala lineare per l'energia cinetica.

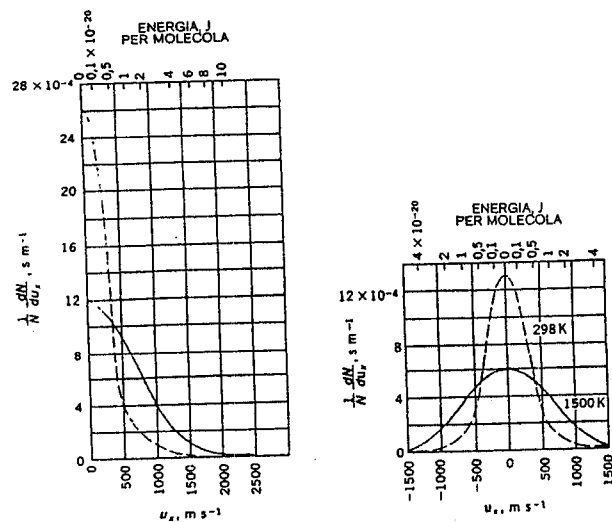


Figura 2.5.
La distribuzione (a) delle velocità e (b) delle velocità nella direzione delle x , per molecole di N_2 .

Si può facilmente definire anche la distribuzione della componente del vettore velocità nella direzione x , ovvero la distribuzione sia delle intensità che delle direzioni. La distribuzione nella direzione $+x$ sarà uguale a quella nella direzione $-x$, per cui le curve di distribuzione della velocità possono essere tracciate partendo da quelle riportate in Fig. 2.5. a, dividendo i valori delle ordinate per 2, e riportando nello stesso diagramma, sia la parte positiva che quella negativa come è stato fatto nella Fig. 2.5. b. L'espressione analitica corrispondente a tali curve di distribuzione è data da:

$$\frac{dN}{N} = \sqrt{\frac{m}{2\pi kT}} e^{-(1/2) mu_x^2 / kT} \quad [29]$$

2.6. Distribuzione di velocità molecolari nello spazio

Sorvoliamo ora sulla distribuzione delle velocità molecolari nel piano e procediamo direttamente a considerare il più importante caso di distribuzione nello spazio. Di nuovo grazie alla distribuzione di Boltzmann avremo i mezzi per ricavare un'espressione della distribuzione. L'espressione che ricaveremo è stata ottenuta per la prima volta da James Clark Maxwell ed è comunemente nota come espressione di *distribuzione di Maxwell-Boltzmann*. Nel caso unidimensionale che abbiamo appena visto, consideriamo la densità dei punti lungo una qualsiasi direzione, per esempio la direzione dell'asse delle x .

Dalla Fig. 2.3., sebbene essa sia costruita con un modesto numero di punti, si può osservare che i punti contenuti in un elemento di volume, du_x , escono da esso quando viene spostato in una direzione o nell'altra rispetto all'origine. In tal modo, naturalmente, è possibile considerare distribuzioni unidimensionali di u_y e u_z lungo gli assi y e z . Queste distribuzioni unidimensionali possono essere combinate per dare la frazione di molecole che hanno componenti di velocità tra u_x e $u_x + du_x$, u_y e $u_y + du_y$, u_z e $u_z + du_z$. Essa è uguale alla frazione di punti che si trova nell'elemento cubico di volume disegnato in Fig. 2.6. ed è analiticamente espressa come il prodotto delle frazioni di molecole che si trovino in appropriati elementi di volume perpendicolari agli assi. Possiamo così scrivere:

$$\frac{dN}{N} = \left(\sqrt{\frac{m}{2\pi kT}} e^{-(1/2) mu_x^2 / kT} du_x \right) \left(\sqrt{\frac{m}{2\pi kT}} e^{-(1/2) mu_y^2 / kT} du_y \right) \left(\sqrt{\frac{m}{2\pi kT}} e^{-(1/2) mu_z^2 / kT} du_z \right)$$

oppure:

$$\frac{dN}{N} = \left(\frac{m}{2\pi kT} \right)^{3/2} e^{-(1/2) m (u_x^2 + u_y^2 + u_z^2) / kT} du_x du_y du_z \quad [30]$$

Questa espressione dà la distribuzione delle velocità molecolari, esprimendo la densità dei punti nell'elemento di volume di Fig. 2.6.

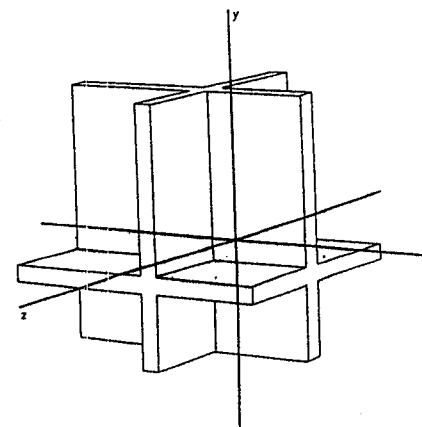


Figura 2.6.
Elementi di volume che sono combinati nella distribuzione di $(dN/N) du_x du_y du_z$.

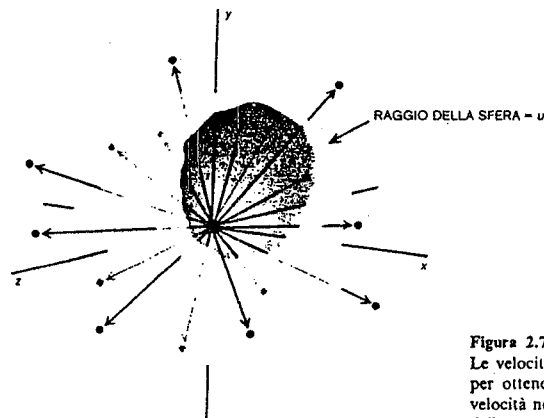


Figura 2.7.
Le velocità molecolari e l'elemento di volume usato per ottenere la distribuzione dell'intensità delle velocità nelle tre dimensioni dello spazio. Il volume dello strato sferico è $4\pi u^2 du$.

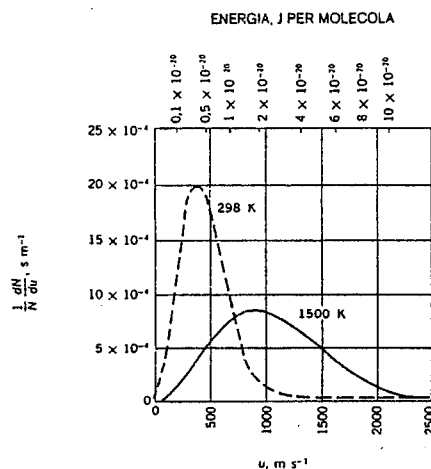


Figura 2.8.
Le distribuzioni di velocità delle molecole di N_2 a 298 e 1500 K.

Quello che si cerca, comunque, è la densità dei punti in un elemento di volume come quello della Fig. 2.7. in quanto tutti i punti che si trovano in un tale elemento hanno la stessa velocità u . Il volume di questa sottile crosta sferica si può scrivere come $4\pi u^2 du$ e per ottenere il numero dei punti che risiedono in questo volume si moltiplica il coefficiente dell'elemento di volume dell'Eq. [30] per $4\pi u^2 du$ invece che per du_x, du_y, du_z . In tal modo e con le sostituzioni $u^2 = u_x^2 + u_y^2 + u_z^2$, si ottiene l'equazione di distribuzione delle velocità nello spazio:

$$\frac{dN/N}{du} = 4\pi \left(\frac{m}{2\pi kT} \right)^{3/2} e^{-(1/2) mu^2/kT} u^2 \quad [31]$$

Questa relazione detta di Maxwell-Boltzmann viene illustrata per l'azoto nel diagramma in Fig. 2.8. a due diverse temperature. La velocità media ha un valore che, come si può immediatamente osservare, è simile a quello precedentemente calcolato per la velocità quadratica media. Si può anche notare che, a bassa temperatura, le molecole tendono ad avere velocità contenute in una banda relativamente ristretta. A più alte temperature la distribuzione è più ampia; inoltre, la curva si mantiene elevata per più alte velocità e ciò è assai importante per alcuni scopi.

La conoscenza della curva di distribuzione consente il calcolo di qualsiasi tipo di media.

quadratica media, che è già stata ricavata con altri sistemi nel paragrafo 2.4., per giungere al valore:

$$\sqrt{u^2} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3RT}{M}}$$

Per ottenere medie di questo tipo, dall'espressione di distribuzione, si moltiplica la frazione di molecole, che hanno un certo valore della quantità da mediare, per il valore stesso e poi si sommano o integrano tutti i possibili valori della quantità. Così u^2 è dato da:

$$\begin{aligned} \overline{u^2} &= \int_{u=0}^{u=\infty} u^2 \frac{dN}{N} \\ &= 4\pi \left(\frac{m}{2\pi kT} \right)^{3/2} \int_0^\infty u^4 e^{-(1/2) mu^2/kT} du \end{aligned}$$

Si usa poi uno degli integrali dell'Appendice 1 per ottenere:

$$\overline{u^2} = 4\pi \left(\frac{m}{2\pi kT} \right)^{3/2} \left(\frac{2kT}{m} \right)^{5/2} \frac{3}{8} \sqrt{\pi} = \frac{3kT}{m} \quad [32]$$

Infine, si ricava $\sqrt{u^2} = \sqrt{3kT/m}$, come già ottenuto nel paragrafo 2.4. dalla teoria cinetica molecolare. In modo simile si ottiene la velocità media come:

$$\bar{u} = \int_{u=0}^{u=\infty} u \frac{dN}{N}$$

La sostituzione della relazione di distribuzione e la valutazione dell'integrale danno il risultato seguente:

$$\bar{u} = \sqrt{\frac{8kT}{\pi m}} = \sqrt{\frac{8RT}{\pi M}} \quad [33]$$

Infine, talvolta, può essere utile impiegare la velocità più probabile, che è la velocità corrispondente al massimo delle curve di Fig. 2.8. Per determinare questa velocità è sufficiente valutare la derivata dell'espressione di distribuzione, uguagliarla a zero e definire il valore di u che soddisfa all'uguaglianza ottenuta. Così, se α indica la velocità più probabile, si ha:

$$\alpha = \sqrt{\frac{2kT}{m}} = \sqrt{\frac{2RT}{M}} \quad [34]$$

Le tre espressioni di velocità: la radice quadrata della velocità quadratica media, la velocità media e quella più probabile non sono molto diverse e i loro rapporti sono dati da:

$$\sqrt{u^2} : \bar{u} : \alpha = 1,00 : 0,92 : 0,82 \quad [35]$$

L'una o l'altra di queste velocità fornisce, di solito, informazioni sufficienti sulla velocità delle molecole in un qualsiasi problema.

Dove è richiesta una più rigorosa conoscenza della distribuzione di velocità molecolari bisogna ricorrere all'espressione di distribuzione o a grafici come quelli riportati in Fig. 2.8. Grazie all'applicazione della distribuzione di Boltzmann abbiamo imparato molto di più sulle velocità con cui si muovono le molecole, rispetto a quanto conosceamo in precedenza, unicamente da una analisi delle relazioni: $Pv = 1/3 Nmu^2$ e $Pv = RT$. Impiegando, inol-

tre, la distribuzione delle velocità molecolari per ricalcolare $\sqrt{u^2}$, abbiamo verificato che quanto espresso in questo paragrafo è in perfetto accordo con i risultati della teoria cine-

2.7. Effusione e raggi molecolari

La maggior parte dei fenomeni che abbiamo finora osservato dipendeva da proprietà tridimensionali medie delle molecole, appartenenti a un campione di gas. La pressione è un esempio tipico di tali proprietà. Alcuni fenomeni però, dipendono, in modo più stretto dagli urti delle molecole di un gas contro una superficie, ad esempio, nel caso dell'adsorbimento e della catalisi eterogenea. Alcuni fenomeni dipendono, inoltre, dal passaggio delle molecole di un gas attraverso un orifizio o una fessura nella parete di un recipiente, come nel caso dell'effusione e dei raggi molecolari. In questi casi non è sufficiente conoscere le velocità delle molecole del gas così come si è fatto finora, ma sono necessarie ulteriori considerazioni che verranno ora riportate.

I fasci molecolari forniscono attualmente una valida tecnica per studiare le proprietà e le reazioni delle molecole e ne verrà ora esposta una analisi svolta alla comprensione di alcune delle caratteristiche delle molecole.

Si ottiene un fascio quando un gas viene fatto fluire attraverso un piccolo foro nella parete di un recipiente, verso un ambiente esterno che si trova sotto vuoto spinto, in modo tale che gli urti molecolari non siano frequenti. Le molecole si muovono, allora, secondo linee rette e con opportuni ostacoli si può selezionare un fascio di molecole.

Calcoliamo, innanzitutto, la velocità media delle molecole di un tale fascio, che consideriamo diretto nella direzione positiva delle x .

L'informazione necessaria per questo calcolo si può ricavare dalla Fig. 2.5. o dall'Eq. [29].

L'Eq. [29] dà la frazione di tutte le molecole con componente di velocità nella direzione delle x fra u_x e $u_x + du_x$. Così la media richiesta delle molecole che hanno una componente della velocità nella direzione delle x è:

$$\bar{u}_{x(+)} = \frac{\int_0^{\infty} u_x \frac{dN/N}{du_x} du_x}{\int_0^{\infty} \frac{dN/N}{du_x} du_x}$$

o con l'Eq. [29]:

$$\bar{u}_{x(+)} = \frac{\sqrt{\frac{m}{2\pi kT}} \int_0^{\infty} u_x e^{-(1/2)mu_x^2/kT} du_x}{\sqrt{\frac{m}{2\pi kT}} \int_0^{\infty} e^{-(1/2)mu_x^2/kT} du_x}$$

Il denominatore esprime la frazione di molecole aventi la componente della velocità nella direzione positiva di x , ed ha il valore di $1/2$, ottenuto mediante gli integrali dell'Appendice 1.

La valutazione del numeratore, fatta usando nuovamente gli integrali dell'Appendice 1, dà poi:

$$\bar{u}_{x(+)} = \sqrt{\frac{2kT}{\pi m}}$$

e con $\bar{u} = \sqrt{8kT/\pi m}$ dal paragrafo 2.6. Possiamo allora scrivere:

$$\bar{u}_{x(+)} = \frac{1}{2} \bar{u} \quad [36]$$

Poiché le distribuzioni di velocità nelle direzioni x , y , e z sono indipendenti l'una dall'altra, il risultato $\bar{u}_{x(+)} = 1/2 \bar{u}$ si applica sia alle molecole che si muovono caoticamente in un recipiente in tutte le direzioni, sia alle molecole con direzione univoca, come nel caso dei fasci molecolari.

Grazie a questo fatto siamo in grado di ottenere una equazione dell'effusione che definisca la velocità con cui le molecole usciranno da un foro nella parete di un recipiente, quando la pressione del gas sia sufficientemente bassa e il foro sia sufficientemente piccolo, perché le molecole passino con un flusso che si possa considerare costituito da singole molecole.

Consideriamo un'area unitaria della parete del recipiente. Quante molecole al secondo urteranno contro quest'area; o se l'area in questione è un foro, quante molecole vi passeranno? Se vi sono N^* molecole per centimetro cubico, $N^*/2$ si muovono nella direzione positiva delle x . Il numero di molecole che raggiunge la superficie di area unitaria, per secondo, è uguale al numero di esse contenute nella regione con area trasversale unitaria e lunghezza $\bar{u}_{x(+)} = \bar{u}/2$. Così:

$$\text{velocità di effusione} \quad \frac{N^*}{2} \bar{u}_{x(+)} = \frac{1}{2} N^* \bar{u}$$

oppure

$$\text{velocità di effusione} = N^* \sqrt{\frac{kT}{2\pi m}} = N^* \sqrt{\frac{RT}{2\pi M}} \quad [37]$$

Quest'ultima costituisce l'importante equazione della effusione esprime la velocità con cui le molecole di un gas si allontanano in un processo effusivo.

La relazione è in accordo con la legge empirica di Graham in cui il numero di molecole che fuoriescono da un orifizio, per unità di tempo, è inversamente proporzionale alla radice quadrata delle masse molecolari. Il comportamento non ideale dei gas, come nel caso di altre espressioni relative al gas ideale, rende non vera sia la dipendenza della massa sia quella prevista dalla temperatura.

(Spesso si asserisce che l'equazione si può applicare e si deve considerare valida anche quando in effetti non sussistano le condizioni per l'effusione molecolare, ciò consegue al fatto che i processi diffusivi, che consistono in un flusso di gas, con urti fra le molecole e contro le pareti, dipendono dalle stesse variabili dei processi effusivi.)

Si dovrebbe osservare, infine, che l'Eq. [36] dà non solo la media delle velocità, nella direzione delle x , delle molecole che fuoriescono e si muovono all'esterno con velocità variabili nella direzione y e z , ma anche di quelle che vengono selezionate con un apposito sistema a fessura, per avere piccole velocità nelle direzioni y e z e per formare così un fascio molecolare nella direzione delle x .

2.8. Libero cammino medio, diametro di collisione e numero di collisione

Abbiamo potuto considerare, finora, le molecole come costituite da punti, ne abbiamo perciò ignorato le dimensioni e la possibilità che subiscano urti reciproci. Pertanto, il significato di pressione esercitata da un gas, espresso nel paragrafo 2.2., si basava sull'idea che le molecole rimbalzassero avanti e indietro fra le pareti del recipiente. Vedremo che, a eccezione del caso di un gas a pressione molto bassa, una molecola nell'attraversare il recipiente subisce molti urti con le altre molecole. D'altronde, poiché questi urti lasciano inalterata la quantità di moto delle molecole che si urtano, nella direzione che si considera, queste collisioni non hanno alcuna influenza nella deduzione per via teorica della legge della pressione di un gas. Ciò comporta però che sia impossibile ottenere delle informazioni su questi urti mediante calcoli sulla pressione dei gas, simili a quelli del paragrafo 2.2.

Nel paragrafo 2.9. vedremo che la viscosità di un gas dipende, in realtà, proprio dagli urti fra una molecola e l'altra.

Una derivazione della viscosità dei gas, secondo la teoria cinetica molecolare, perciò, fornirà ulteriori informazioni sul rapido movimento delle molecole.

Tre domande sorgono spontanee sulle proprietà legate alla collisione fra le molecole di un gas. Quale distanza, ad esempio, intercorre fra un urto e il successivo? Quanti urti per secondo subisce una molecola in media? Quanti urti per secondo hanno luogo in un certo volume di gas?

Quando cerchiamo di rispondere a queste domande ci accorgiamo di quanto ci sia poco familiare il mondo molecolare.

Prima di procedere al calcolo delle viscosità dei gas, mostriamo che la risposta a queste tre domande è legata a una proprietà molecolare e precisamente al diametro delle molecole

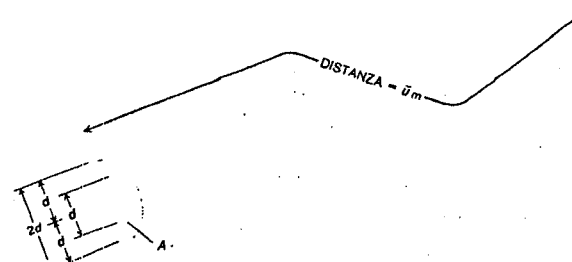


Figura 2.9. Cammino percorso da una molecola A in 1 s. Le molecole vengono rappresentate molto ingrandite rispetto alla distanza fra esse, e nelle condizioni di temperatura a pressione standard, si verificano molte più collisioni nell'intervallo di 1 s.

gassose. L'uso del diametro, per definire la dimensione delle molecole, significa attribuire loro una forma sferica e inoltre significa che le dimensioni effettive delle molecole sono indipendenti dall'energia in gioco negli urti molecolari. Le molecole sono considerate come sfere rigide senza mutua attrazione.

Consideriamo una particolare molecola A , in Fig. 2.9., che si muova in una certa direzione. Se la velocità della molecola A è \bar{u} , essa si muoverà per una distanza di \bar{u} m in 1 s. Inoltre, se si considera solo A in movimento e tutte le altre molecole restano ferme, la molecola A urterà in 1 s tutte le molecole che hanno i loro centri entro il cilindro della Fig. 2.9. Il volume del cilindro, il cui raggio è uguale al diametro molecolare è $\pi d^2 \bar{u}$.

Il numero di molecole contenute nel cilindro è $\pi d^2 \bar{u} N^*$, dove N^* è il numero di molecole per metro cubo. Il libero cammino medio, cioè la distanza coperta fra due urti successivi costituisce la lunghezza del cilindro, \bar{u} , diviso il numero degli urti che avvengono quando la molecola percorre questa distanza. Così, se si introduce L , per indicare la lunghezza del libero cammino:

$$L = \frac{\bar{u}}{\pi d^2 \bar{u} N^*} = \frac{1}{\pi d^2 N^*} \quad [38]$$

Un calcolo più rigoroso dimostra che questa relazione non è corretta. L'assunzione che solo A si muova implica che la velocità relativa delle molecole urtate sia \bar{u} . Infatti, come la Fig. 2.10. suggerisce, se le molecole si muovono tutte con velocità \bar{u} , si verificano tutti i tipi di urti, che vanno da collisioni, in cui la velocità relativa è molto piccola, a collisioni testa-testa dove la velocità relativa è $2\bar{u}$. In media in un urto si verifica che le molecole si muovano ad angolo retto l'una rispetto all'altra, e quindi la velocità relativa è espressa da $\sqrt{2}\bar{u}$. Si può scrivere allora al posto dell'Eq. [38] una relazione corretta se si tiene conto che, sebbene la molecola A si muova per una distanza \bar{u} in 1 s, essa urta con altre molecole con una velocità relativa di $\sqrt{2}\bar{u}$. Il libero cammino medio diventa perciò:

$$L = \frac{1}{\sqrt{2} \pi d^2 N^*} \quad [39]$$

La risposta alla prima domanda che ci eravamo posti, cioè, qual è la distanza che una molecola copre fra un urto e il successivo, dipende, come si è visto, dal numero delle molecole per unità di volume e da una certa grandezza che ancora non conosciamo.

Il secondo problema da risolvere era il calcolo del numero di urti per secondo che una molecola subisce. Questo dato viene definito *numero di collisione* e indicato con Z_1 .

La molecola A si muove, rispetto alle altre molecole, con una velocità effettiva uguale a $\sqrt{2}\bar{u}$. Il numero di urti per secondo di questa molecola sarà pertanto uguale al numero di molecole contenute in un cilindro di raggio d e di lunghezza $\sqrt{2}\bar{u}$. Abbiamo allora:

$$\begin{aligned} Z_1 &= (\sqrt{2}\bar{u}) (\pi d^2) N^* \\ &= \sqrt{2} \pi d^2 \bar{u} N^* \end{aligned} \quad [40]$$

L'ultimo dei tre problemi da risolvere consiste nella determinazione del numero di urti che si verificano nell'unità di volume, per unità di tempo. Come si può immaginare questa grandezza è di considerevole importanza per comprendere il significato della velocità delle reazioni chimiche. Il numero di urti per secondo e per metro cubo viene anch'esso chiamato numero di collisione, ma è indicato con Z_{11} .

Il numero di collisione Z_{11} è in stretta relazione con il numero Z_1 . Poiché in un metro cubo

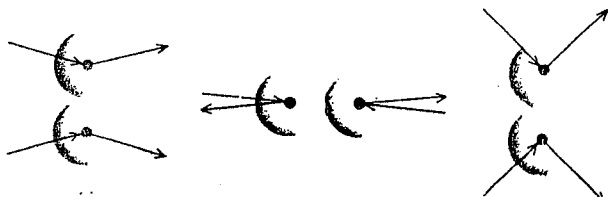


Figura 2.10.
Tipi di urti molecolari.
La velocità relativa in una collisione media è $\sqrt{2}\bar{u}$.
(a) Velocità relativa $\cong 0$
(b) Velocità relativa $= 2\bar{u}$

sono contenute N^* molecole e ciascuna di queste subisce Z_1 urti per secondo, il numero totale di urti per secondo e per metro cubo sarà $1/2 N^* Z_1$. Il fattore $1/2$ viene introdotto perché ciascun urto non venga contato due volte. Si otterrà allora:

$$\begin{aligned} Z_{11} &= \frac{1}{2} \sqrt{2} \pi d^2 \bar{u} (N^*)^2 \\ &= \frac{1}{\sqrt{2}} \pi d^2 \bar{u} (N^*)^2 \end{aligned} \quad [41]$$

Sia i numeri di collisione, che il libero cammino medio, sono stati definiti con equazioni che contengono il diametro molecolare d . Poiché le velocità molecolari ed il numero di molecole per metro cubo di un particolare gas sono delle quantità determinabili, per valutare L , Z_1 e Z_{11} , è necessario conoscere soltanto i diametri molecolari.

Come vedremo, vi sono molti metodi per determinare le dimensioni molecolari. Per il momento questi valori si otterranno ricavando, per via teorica, la viscosità dei gas mediante la teoria cinetica molecolare.

2.9. Teoria cinetica della viscosità dei gas

La teoria cinetica molecolare secondo cui le molecole si muovono liberamente in ogni direzione con grandi spazi tra una molecola e l'altra, sembrerebbe a prima vista escludere completamente la presenza di forze viscosi.

L'azione di freno, esercitata dalla viscosità, si può studiare focalizzando l'attenzione su due strati di gas che si muovano l'uno parallelamente all'altro, ma a diverse velocità di flusso. Oltre al loro caotico moto termico, le molecole nello strato che si muove più velocemente, avranno una componente di velocità nella direzione del flusso, più grande rispetto alle molecole che si trovano, invece, nello strato più lento. Ma a causa del loro moto disordinato, alcune delle molecole dello strato più veloce andranno a finire nello strato più lento, portando un contributo addizionale alla quantità di moto nella direzione del flusso aumentando così la velocità. Allo stesso modo alcune molecole dello strato più lento raggiungeranno lo strato più veloce e tenderanno a farlo rallentare. L'effetto globale di questo scambio di molecole si manifesta in una tendenza delle diverse parti del gas ad attenuare le differenze nella velocità di flusso. L'effetto viscoso costituisce propriamente la difficoltà di muovere una parte di fluido rispetto a un altro.

Su questa base si può elaborare una teoria cinetica-molecolare semplificata della viscosità. Consideriamo due strati di area unitaria, separati da una distanza pari al libero cammino medio, di un gas che fluisce come in Fig. 2.11. Il gas fluisce nella direzione delle x con una

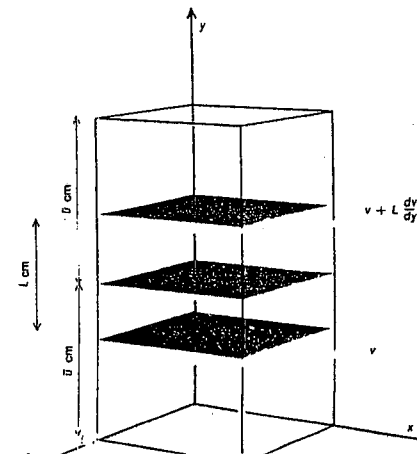


Figura 2.11.
Due strati di un gas che si muovono nella direzione

ogni incremento della distanza dy , nella direzione delle y .

Poiché gli strati in considerazione distano fra loro di una distanza pari al libero cammino medio, in media una molecola che lascia uno strato arriverà nell'altro e qui urterà delle molecole contribuendo ad aumentare o a diminuire la quantità di moto nella direzione del flusso di quello strato. Secondo un modo semplice di affrontare il problema, che dà un risultato quasi corretto; un terzo delle molecole ha una componente lungo l'asse x della velocità, un terzo una componente lungo l'asse y e un terzo una componente lungo l'asse z . Solo quel terzo che ha la componente lungo l'asse y può influenzare il cambiamento delle quantità di moto fra i due strati.

La variazione positiva o negativa della quantità di moto, per effetto di una molecola che si trasferisce nel nuovo strato è data da $mL (dv/dy)$; cioè m volte la differenza della velocità dei due strati. Si può calcolare nuovamente la forza tra i due strati, dalla velocità con cui varia la quantità di moto. È ora necessario perciò calcolare il numero di molecole che si trasferisce da uno strato all'altro per secondo.

Il numero di molecole che lasciano lo strato più basso e quelle che scendono dal più alto in 1 s, è uguale a quello delle molecole che si trovano nel volume più basso con componente della velocità diretta verso l'alto, in direzione y , e a quello delle molecole che si trovano nel volume in alto e hanno un componente di velocità diretta in basso, sempre nella direzione delle y . Questi due volumi sono entrambi segnati in Fig. 2.11. con una lunghezza uguale a $\bar{u}m$, cosicché, in 1 s tutte le molecole che hanno la direzione adeguata avranno attraversato la sezione trasversale indicata con una zona ombreggiata. Se ci sono N^* molecole per metro cubo, ci saranno $1/6 N^* \bar{u}$ molecole nel volume più basso, che si sposteranno tutte nel volume più alto in 1 s.

Un numero simile si muoverà dall'alto, verso il volume in basso, sempre in 1 s. L'interscambio tra i due strati sarà perciò $1/3 N^* \bar{u} s^{-1}$.

La velocità con cui varia la quantità di moto è data, allora, da $(1/3 N^* \bar{u}) mL (dv/dy)$, e per la legge di Newton, si identifica con la forza esercitata dagli strati, l'uno sull'altro. Così:

$$f = \frac{1}{3} N^* \bar{u} mL \frac{dv}{dy} \quad [42]$$

Il coefficiente di viscosità η è stato precedente definito mediante l'Eq. [26] del Capitolo 1; in forma differenziale e per aree unitarie degli strati, si può scrivere come segue:

$$f = \eta \frac{dv}{dy} \quad [43]$$

Un confronto fra queste equazioni dà per la viscosità, interpretata dal punto di vista cinetico molecolare il seguente risultato:

$$\eta = \frac{1}{3} N^* \bar{u} mL \quad [44]$$

Una derivazione più rigorosa tiene conto della distribuzione delle velocità molecolari e porta a una espressione leggermente diversa:

$$\eta = \frac{1}{2} N^* \bar{u} mL \quad [45]$$

Questa espressione verrà impiegata per dedurre alcune delle proprietà molecolari quali d , L , Z_1 , Z_{11} .

È ora conveniente sostituire L mediante l'Eq. [39], in modo da ottenere un'espressione legata al diametro di collisione.

$$\eta = \frac{\bar{u}m}{2\sqrt{2}\pi d^2} \quad [46]$$

Questa importante relazione consente il calcolo del diametro di collisione di una molecola gassosa, da misure di viscosità del gas. È necessario avere anche i valori della massa di una molecola di gas e della velocità media delle molecole del gas. Entrambe queste quantità sono disponibili, l'ultima come risultato dell'espressione del paragrafo 2.6.

$$\bar{u} = \sqrt{\frac{3RT}{\pi M}}$$

Prima di procedere a una discussione sui valori delle proprietà molecolari che sono state introdotte nel paragrafo 2.8. è interessante porre in evidenza un aspetto dell'Eq. [46] sulla natura della viscosità dei gas. Per un certo gas, m e d sono costanti, e \bar{u} varia con la radice quadrata di T , secondo l'Eq. [47]. L'espressione ottenuta per via teorica prevede, perciò, che la viscosità di un gas sarà indipendente dalla pressione e proporzionale alla radice quadrata della temperatura assoluta. Questa constatazione piuttosto importante (semberebbe ragionevole pensare che la viscosità dovesse aumentare con la pressione, poiché un gas compresso diventa più denso), fu una delle poche deduzioni teoriche che precedette qualsiasi misura sperimentale. La predizione fatta da Maxwell di tale comportamento e la successiva verifica sperimentale, costituì uno dei più notevoli trionfi della teoria cinetica molecolare. (Vale la pena, comunque, di ricordare che alle pressioni più alte il comportamento non ideale dei gas interferisce seriamente fino a non rendere più vere le relazioni dedotte).

2.10. Valori numerici delle proprietà di collisione

Consideriamo come esempio esplicativo il calcolo delle proprietà di collisione d , L , Z_1 e Z_{11} per N_2 a 1 atm e 25 °C. La Tab. 1.4. dà il valore della viscosità:

$$\eta = 1,78 \times 10^{-4} \text{ poise} = 1,78 \times 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1}$$

Il numero di molecole in 1 m³, a 25 °C, e 1 atm, si ricava dal numero $6,022 \times 10^{23}$ di molecole in 22,414 litri, o $0,022414 \text{ m}^3$, a condizioni normali, nel modo seguente:

$$N^* = \frac{6,022 \times 10^{23}}{0,022414} \times \frac{273,15}{298,15} = 2,461 \times 10^{25} \text{ m}^{-3}$$

La media delle velocità molecolari è data da:

$$\bar{u} = \sqrt{\frac{(8)(8,314)(298,15)}{\pi \times 0,02802}} = 0,475 \times 10^3 \text{ m s}^{-1}$$

e la massa di una molecola è:

$$m = \frac{0,02802}{6,022 \times 10^{23}} = 4,65 \times 10^{-26} \text{ kg}$$

Con questi dati si può calcolare il diametro di collisione della molecola di N_2 dopo aver opportunamente riarrangiato l'Eq. [46]:

$$d = \sqrt{\frac{\bar{u}m}{2\sqrt{2}\pi\eta}} = 3,74 \times 10^{-10} \text{ m}$$

Usando questo valore del diametro molecolare e le equazioni dalla [39] alla [41], si possono calcolare la rimanenti proprietà collisionali, per N_2 , nelle condizioni specificate. Così avremo:

$$L = \frac{1}{\sqrt{2}\pi d^2 N^*} = 6,50 \times 10^{-8} \text{ m}$$

$$Z_1 = \sqrt{2}\pi d^2 \bar{u} N^* = 7,31 \times 10^9 \text{ collisioni s}^{-1}$$

$$Z_{11} = \frac{1}{\sqrt{2}}\pi d^2 \bar{u} (N^*)^2 = 8,99 \times 10^{34} \text{ collisioni m}^{-3} \text{ s}^{-1}$$

Tabella 2.2. Alcune proprietà della teoria cinetico-molecolare dei gas (a 25 °C e 1 atm).

	Diametro di collisione d		Libero cammino medio L	Numero di collisione Z_1	Numero di collisione Z_{11}
	(m)	(Å)	(m)	(s ⁻¹)	(m ⁻³ s ⁻¹)
H ₂	$2,73 \times 10^{-10}$	2,73	$12,3 \times 10^{-8}$	$14,4 \times 10^9$	$17,7 \times 10^{24}$
He	2,18	2,18	19,0	6,6	8,1
N ₂	3,74	3,74	6,50	7,3	9,0
O ₂	3,57	3,57	7,14	6,1	7,5
Ar	3,96	3,96	5,80	6,9	8,5
CO ₂	4,56	4,56	4,41	8,6	10,6
HI	3,50	3,50	7,46	3,0	3,7

I dati di Tab. 2.2. danno una indicazione di come si possano definire, grazie alla teoria cinetico-molecolare, alcuni dettagli del mondo molecolare. Questi dati forniscono le basi per intuire molti fenomeni molecolari e vale la pena di fare uno sforzo per acquistare familiarità con gli ordini di grandezza di queste quantità.

Osservate, ad esempio, che le molecole sono in verità assai piccole rispetto al volume occupato da un campione di gas in condizioni normali. Le dimensioni molecolari, come viene messo in evidenza nella Tab. 2.2., sono dell'ordine di 10^{-10} m. Però, nonostante nel mondo molecolare si abbia a che fare con dimensioni così modeste, non vi è alcuna difficoltà nell'abituarsi a pensare in termini di dimensioni molecolari. Un aiuto si può ottenere utilizzando una adeguata unità di lunghezza. L'angstrom (abbreviato Å) è l'unità in cui quasi sempre vengono espresse le dimensioni molecolari. Esso è definito come segue:

$$1 \text{ Å} = 10^{-10} \text{ m}$$

Sebbene l'unità di lunghezza angstrom non appartenga al sistema SI, essa viene usata così spesso ed è così conveniente, per le dimensioni molecolari, che talvolta alcune lunghezze verranno riportate in angstrom. È importante comprendere che i diametri di Tab. 2.2. riflettono il metodo particolare con cui è stata misurata la dimensione delle molecole.

La determinazione del diametro di collisione richiede, innanzitutto, l'assunzione che la molecola sia sferica, in modo tale che la sua dimensione possa essere definita mediante una sola variabile, il diametro. D'altronde, l'aver impiegato solo questo parametro, implica che le molecole vengano considerate come sfere rigide, senza alcuna mutua attrazione. L'effetto che si verifica eliminando questa limitazione verrà descritto in seguito a proposito dello studio della velocità delle reazioni chimiche, nel Capitolo 17.

Il libero cammino medio dei gas a 1 atm di pressione, come si vede dall'esempio per N₂, sebbene sia diverse centinaia di volte più grande del diametro molecolare, è piccolo rispetto alle dimensioni di un comune recipiente.

Le molecole di un gas in un tale recipiente, perciò si urteranno spesso fra loro, prima di urtare le pareti del recipiente. Ma il libero cammino medio, per un certo gas, è inversamente proporzionale al numero di molecole per unità di volume, e così esso è inversamente proporzionale alla pressione. A pressione molto bassa, come avviene nei più alti strati atmosferici, il libero cammino medio può anche essere dell'ordine di alcuni metri, cioè molto molto maggiore dei valori riportati in Tab. 2.2.

Si devono considerare, infine, i numeri di collisione Z_1 e Z_{11} . Nelle condizioni indicate in Tab. 2.2., il numero notevole di urti al secondo, le piccolissime distanze percorse dalle molecole fra un urto e il successivo e le velocità molecolari elevatissime, indicano una naturale attività esistente nel mondo molecolare. A basse pressioni, sebbene le velocità molecolari restino inalterate, diminuisce il numero di urti subito da una molecola nell'unità di tempo, mentre, il numero totale di urti che avvengono in un certo volume di gas diminuisce anche più rapidamente per la dipendenza dall'inverso del quadrato della densità delle particelle

2.11. Teoria del comportamento non ideale - Equazione di van der Waals

Il semplice modello, offerto dalla teoria cinetica molecolare, è soddisfacente in quanto consente di ricavare le leggi dei gas ideali. Abbiamo visto, comunque, che i gas reali manifestano delle relazioni PVT che deviano, in modo più o meno pronunciato, dalle leggi dei gas ideali.

Sorge, allora, naturalmente la domanda sulla possibilità di poter comprendere la natura di queste deviazioni usando per un gas un modello più elaborato di quello impiegato precedentemente. Questo obiettivo si può certamente conseguire e nella nostra ricerca di informazioni sulle molecole è molto interessante indagare quali ritocchi siano necessari al modello precedente.

Nel 1873, il chimico olandese van der Waals dimostrò che l'aggiunta di altri due termini, al modello molecolare del paragrafo 2.1., è sufficiente a spiegare molte delle deviazioni dei gas reali, rispetto al comportamento ideale. Egli attribuì l'insuccesso delle relazioni $PV = nRT$ per spiegare il comportamento dei gas reali al fatto di aver trascurato:

- 1) il volume occupato dalle molecole;
- 2) le forze di attrazione fra le molecole.

Le correzioni introdotte, che tengono conto di questi due fattori, saranno considerate una alla volta.

Quando n moli di un gas sono contenute in un recipiente di volume V , il volume in cui le molecole sono libere di muoversi è uguale a V , solo se il volume occupato dalle molecole stesse è trascurabile. La presenza di molecole che abbiano una dimensione non trascurabile significa che un certo volume, chiamato *covolume* viene sottratto al moto delle molecole. Se il covolume di 1 mole di un gas viene indicato con b , allora invece di scrivere $PV = nRT$, avremo un'equazione più corretta che sarà:

$$P(V - nb) = nRT$$

[48]

Il covolume b viene solitamente considerato una costante caratteristica di ogni gas e deve essere determinato empiricamente per ottenere una precisa correzione della semplice espressione della legge dei gas.

La relazione fra b e la dimensione delle molecole si può mettere in rilievo osservando la Fig. 2.12. Le molecole vengono ancora considerate sferiche e di diametro d . Il volume in cui i centri di due molecole non si possono muovere a conseguenza della reciproca presenza è indicato in Fig. 2.12., dal cerchio leggermente ombreggiato. Il raggio di questa sfera è uguale al diametro molecolare. Il covolume per paio di molecole è $4/3 \pi d^3$. Otteniamo allora:

$$\text{VOLUME MOLECOLARE} = \frac{4}{3} \pi \left(\frac{d}{2}\right)^3 = \frac{1}{8} \left(\frac{4}{3} \pi d^3\right)$$

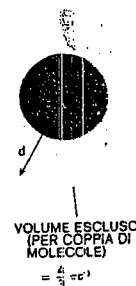


Figura 2.12. Volume escluso (ombreggiato) per una coppia di molecole, secondo la trattazione di van der Waals.

$$\text{volume effettivo di una molecola} = \frac{4}{3} \pi \left(\frac{d}{2} \right)^3$$

$$\text{covolume per molecola} = \frac{1}{2} \left(\frac{4}{3} \pi d^3 \right) = 4 \left[\frac{4}{3} \pi \left(\frac{d}{2} \right)^3 \right]$$

Come si è visto il covolume è quattro volte il volume effettivo delle molecole. Poiché b è il covolume per mole, si avrà:

$$b = 4N \left[\frac{4}{3} \pi \left(\frac{d}{2} \right)^3 \right] \quad [49]$$

dove N è il numero di Avogadro. (Potete notare che questa relazione, da cui si ricava che il covolume, che è quattro volte il volume di tutte le molecole, si applica soltanto se il volume escluso è una conseguenza dell'avvicinamento di due molecole. A pressioni del gas piuttosto elevate può avvenire che più molecole si trovino in posizione adiacente rispetto a una certa molecola e il covolume per molecola si riduce. Quindi molte molecole vengono avvicinate il più possibile le une alle altre, il volume che viene occupato e quindi, non disponibile per le altre molecole, è 1,35 volte il volume effettivo delle molecole).

Potremmo essere tentati di usare i valori di d , prima determinati, per calcolare b . È meglio, comunque, adattare b in modo tale che l'equazione che ne deriva corrisponda il meglio possibile ai dati PVT osservati. Questo procedimento consegue principalmente dalle difficoltà causate dal secondo termine correttivo e fa sì che l'equazione di van der Waals sia un'equazione semiempirica. In altri termini, la forma dell'equazione è ricavata grazie a considerazioni teoriche, mentre i valori numerici delle costanti, che appaiono nelle equazioni, vengono ottenute dai dati PVT sperimentali. Le equazioni semiempiriche sono comuni in chimica e spesso sono assai più soddisfacenti delle relazioni completamente empiriche.

Il secondo termine correttivo di van der Waals riguarda le forze di attrazione intermolecolari. Che esistano tali forze è chiaramente dimostrato dalla tendenza di tutti i gas a condensare a temperature sufficientemente basse affinché tali forze abbiano il sopravvento sull'energia cinetica delle molecole. Mentre è evidente che queste forze di attrazione esistano, è assai difficile avere un'esatta conoscenza delle loro origini e della loro entità quantitativa. La trattazione semiempirica, comunque, richiede soltanto che venga introdotto un termine adeguato a rappresentare tali forze attrattive. Il valore di questo termine si può ottenere per approssimazioni successive, analogamente a b , per poter disporre di un'equazione che si accordi il più possibile con i dati sperimentali PVT .

Una molecola interagisce con una forza attrattiva nei riguardi delle altre molecole vicine; in tal modo l'attrazione agisce, unitamente alla resistenza alla pressione esercitata dalle pareti del recipiente, per tenere insieme le molecole. Una analisi completa delle conseguenze di questo fatto presenta delle difficoltà; qualitativamente l'effetto è di limitare l'indipendenza di ciascuna molecola. La pressione esercitata dal gas viene così ridotta, come se diminuisse il numero di molecole indipendenti. Il contributo di una molecola nel tenere insieme il gas mediante queste forze di attrazione è proporzionale al numero di molecole a essa vicine, con cui può direttamente interagire. Se ci sono n moli di gas in un volume V , tale numero è proporzionale a n/V , cioè al numero di moli per unità di volume. Poiché ciascuna delle molecole vicine a sua volta attrae le altre molecole intorno a essa, l'effetto globale delle forze attrattive è proporzionale a $(n/V)^2$.

Al confinamento di un gas, in una data regione, contribuiscono, pertanto, non solo la pressione esterna P , ma anche le attrazioni intermolecolari, mediante un termine proporzionale a $(n/V)^2$. Se il fattore di proporzionalità viene indicato con a , l'equazione completa di van der Waals diventa:

$$\left(P + \frac{an^2}{V^2} \right) (V - nb) = nRT \quad [50]$$

La capacità di questa equazione nel descrivere il comportamento PVT dei gas reali va giudicata dalla scelta dei valori di a e b , che debbono essere diversi per ciascun gas e per ciascuna temperatura, e che debbono dare il migliore accordo possibile con i dati osservati. Sebbene gli accordi che si ottengono fra i volumi calcolati e quelli osservati non siano perfetti, in un

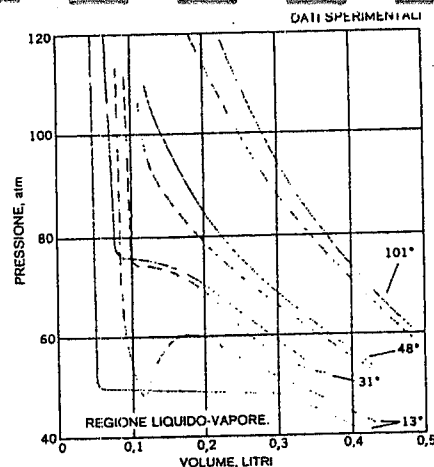


Figura 2.13. Confronto tra le curve PV di van der Waals per CO_2 e i dati sperimentali nei pressi del punto critico.

vasto campo di pressioni l'impiego della [50] porta a un miglioramento assai grande rispetto all'espressione valida per gas ideali: $PV = nRT$. La Fig. 2.13. e la Tab. 2.3. mettono in evidenza l'entità del miglioramento che si ottiene quando si consideri una zona di comportamento non ideale.

Tabella 2.3. Volumi molari di CO_2 a 320 K.

Confronto fra l'equazione di van der Waals e la legge ideale dei gas, nei pressi del punto critico.

P (atm)	v (litri)		
	Osservato	van der Waals	Ideale
1	26,2	26,2	26,3
10	2,52	2,53	2,63
40	0,54	0,55	0,66
100	0,098	0,10	0,26

La validità dell'equazione di van der Waals, nel rappresentare il comportamento PVT , è molto superiore di quanto ci si aspetterebbe da una qualsiasi espressione puramente empirica contenente due sole costanti adattabili.

Il comportamento nella regione in cui siano presenti due fasi, come è mostrato in Fig. 2.13., non può essere descritto con l'equazione di van der Waals, per cui i massimi e minimi delle curve non devono essere considerati.

2.12. Equazione di van der Waals e punto critico

Come mostra la Fig. 2.13., l'equazione di van der Waals segue ragionevolmente bene il comportamento di un gas vicino alla zona di equilibrio liquido-vapore. Esisterà, pertanto, una particolare temperatura a cui l'equazione di van der Waals con opportuni valori di a e b , rivelerà la presenza di una curva, detta isoterma critica con un flesso orizzontale. Questa identificazione fornisce un metodo conveniente, che però non è sempre il più soddisfacente, per ottenere dei valori di a e b .

L'equazione [50] può essere rimaneggiata e scritta per 1 mole:

$$P = \frac{RT}{v - b} - \frac{a}{v^2}$$

$$\frac{dP}{dv} = \frac{-RT}{(v-b)^2} + \frac{2a}{v^3} \quad [52]$$

e

$$\frac{d^2 P}{dv^2} = \frac{2RT}{(v-b)^3} - \frac{6a}{v^4} \quad [53]$$

Al punto critico la derivata prima e la seconda sono nulle, mentre la pressione, il volume molare e la temperatura si scrivono come P_c , v_c e T_c . A questo punto, le Eq. dalla [51] alla [53] diventano rispettivamente:

$$P_c = \frac{RT_c}{v_c - b} - \frac{a}{v_c^2} \quad [54]$$

$$0 = \frac{-RT_c}{(v_c - b)^2} + \frac{2a}{v_c^3} \quad [55]$$

e

$$0 = \frac{2RT_c}{(v_c - b)^3} - \frac{6a}{v_c^4} \quad [56]$$

Queste tre equazioni possono essere risolte per a , b , e R in termini di P_c , v_c e T_c . (La costante dei gas R , naturalmente, è meglio ricavarla con altri mezzi, ma essa compare nell'equazione di van der Waals come se fosse un'altra costante adattabile). Dopo alcuni passaggi si ottengono le seguenti relazioni:

$$b = \frac{1}{3} v_c \quad [57]$$

$$a = 3P_c v_c^2 \quad [58]$$

$$R = \frac{8P_c v_c}{3T_c} \quad [59]$$

$$R = 0.082$$

Con queste relazioni, si possono usare i dati critici della Tab. 1.3. per ricavare dei valori delle costanti di van der Waals a e b e i valori del parametro R , riassunti in Tab. 2.4. Nella tabella

Tabella 2.4. Valori per le costanti a , b , e R dell'equazione di van der Waals. Calcolati dai dati di punto critico di Tab. 1.3. e dalle relazioni delle Eq. [57], [58], [59]. I valori del diametro molecolare sono stati ottenuti mediante l'uso dell'Eq. [49].

Gas	a (atm litri ² mole ⁻²)	b (litri mole ⁻¹)	R (litro atm mole ⁻¹ grado ⁻¹)	Diam. molecolare d (Å)
H ₂	0,162	0,0217	0,067	2,58
He	0,022	0,0192	0,065	2,48
CH ₄	1,33	0,0329	0,063	2,97
NH ₃	1,75	0,0241	0,053	2,67
H ₂ O	1,32	0,0150	0,040	2,29
CO	0,85	0,0300	0,063	2,88
N ₂	0,81	0,0300	0,064	2,88
O ₂	0,82	0,0248	0,064	2,71
CH ₃ OH	3,26	0,0392	0,048	3,15
Ar	0,86	0,0257	0,065	2,74
CO ₂	2,01	0,0319	0,061	2,94
<i>n</i> -C ₃ H ₁₂	9,52	0,1034	0,058	4,35
C ₆ H ₆	9,44	0,0855	0,058	4,08

sono riportati anche i valori di a , b e R calcolati con l'equazione di van der Waals. I valori delle costanti empiriche, calcolate in questo modo, dovrebbero adattare le curve, calcolate con l'equazione di van der Waals ai risultati sperimentali, nelle vicinanze del punto critico. Se il comportamento PVT, in altre zone, è di particolare importanza, potrebbe essere vantaggioso modificare opportunamente i valori di a e b rispetto a quelli calcolati con le Eq. [57] e [58]. Abbiamo visto che i diametri molecolari, calcolati mediante l'equazione di van der Waals, sono approssimativamente in accordo con quelli ottenuti da misure di viscosità e questo risultato ci incoraggia a ritenere che questi numeri rappresentino l'effettivo diametro delle molecole.

Qualche dubbio potrebbe sorgere a proposito dei valori della costante a . È consigliabile però, non affrontare per ora l'argomento delle forze intermolecolari che verrà, invece, considerato nel Capitolo 19.

Nonostante la validità dell'equazione di van der Waals, nel rappresentare il comportamento PVT dei gas reali, spesso impiegheremo la semplice espressione del gas ideale $PV = nRT$. A pressioni basse e temperature non troppo alte, infatti, le deviazioni da questa relazione sono, per molti aspetti, insignificanti. Inoltre, la semplicità dell'espressione precedente e il fatto che essa possa essere impiegata per tutti i gas, senza l'aggiustamento di alcune costanti, ne rendono assai vantaggioso l'impiego.

2.13. L'equazione di van der Waals e la legge degli stati corrispondenti

I dati empirici riportati nel diagramma di Fig. 1.11. mostrano che, in accordo alla legge degli stati corrispondenti, molti gas si comportano in modo simile quando il loro comportamento viene descritto mediante le variabili ridotte P_R , v_R e T_R . È interessante osservare che l'equazione di van der Waals è compatibile con la legge degli stati corrispondenti poiché, se essa viene scritta impiegando le variabili ridotte, non contiene alcuna quantità specifica di un particolare gas che debba essere adattata empiricamente.

Le costanti a , b , e R sono legate alle costanti critiche mediante le Eq. dalla [57] alla [59]. Queste relazioni possono essere sostituite ad a , b e R nell'equazione di van der Waals in modo da ottenere una forma di quest'ultima relazione che contenga esplicitamente le costanti critiche.

Con opportuni passaggi si può ottenere un'equazione in funzione dei soli termini P/P_c , v/v_c e T/T_c . Introducendo le variabili ridotte P_R , v_R e T_R per indicare questi rapporti, per 1 mole di gas abbiamo:

$$\left(P_R + \frac{3}{v_R}\right)\left(v_R - \frac{1}{3}\right) = \frac{8}{3} T_R \quad [60]$$

Si può quindi osservare che l'equazione di van der Waals è in accordo con la legge empirica degli stati corrispondenti. Questa forma della equazione di van der Waals, infatti, si applica senza la valutazione di alcuna ulteriore costante e chiarisce il fatto che, quando si considerano le variabili ridotte, i gas si comportano all'incirca nello stesso modo.

Problemi

- Calcolate la pressione esercitata da 10^{23} particelle di gas, ciascuna di massa 10^{-25} kg, in un recipiente del volume di 1 litro. La radice quadrata della velocità quadratica media è 100 m s^{-1} . Qual è l'energia cinetica totale di queste particelle? Quale deve essere la temperatura?
Ris. $P = 0,33 \text{ atm}$; energia = 50 J ; $T = 24,2 \text{ K}$
- Un bulbo di gas da 1 litro contiene $1,03 \cdot 10^{23}$ molecole di H₂. Se la pressione esercitata da queste molecole è 1 atm, quale deve essere la velocità quadratica media molecolare? Quale deve essere la temperatura?

42. $\frac{1}{2}mv^2$ è l'energia di molecole lasciate in un volume avente la dimensione di una capocchia di spillo, circa 10^{-9} m^3 , quando l'aria viene pompata via fino a ottenere un vuoto di 10^{-9} atm a 25°C .

- 4 Per un campione di gas di N molecole, costituito da N_1 molecole di massa m_1 , e N_2 molecole di massa m_2 , passate attraverso una derivazione simile a quella dei paragrafi 2.2. e 2.3., che conduce alle relazioni $PV = \frac{1}{3} N m \bar{u}^2$ e $PV = nRT$. Quali assunzioni sono necessarie per ottenere la relazione empirica $PV = nRT$ che non dipende dalle masse delle molecole del campione?
- 5 A 25°C calcolate e confrontate le energie cinetiche medie, velocità e quantità di moto delle molecole di He e Hg.
- 6 Calcolate le radici quadrate delle velocità quadratiche medie molecolari degli atomi di He a 10, 100 e 1000 K nelle unità di metri al secondo e miglia per ora (vedi Tab. 2.1.). Se si fissa la pressione a 10^{-9} atm , quali valori si dovrebbero ottenere?
- 7 La teoria cinetica molecolare attribuisce a ciascuna particella una energia cinetica media di $\frac{3}{2} kT$. Quale velocità dovrebbero avere delle particelle di vapore acqueo di massa 10^{-15} kg a temperatura ambiente secondo la teoria cinetica molecolare? Confrontate questo valore con la velocità molecolare di Tab. 2.1.
Risp. $3,5 \times 10^{-3} \text{ m s}^{-1}$.
- 8 Quanto calore si deve aggiungere a $3,45 \times 10^{-3} \text{ kg}$ di neon in un bulbo di 10 litri per far salire la temperatura da 0 a 100°C . Di quale rapporto viene cambiata la velocità quadratica media per il mutamento di temperatura?
- 9 Di quanti gradi deve salire la temperatura di 1 mole di acqua, allo stato liquido, per aggiunta di una certa quantità di energia uguale all'energia cinetica traslazionale, a 25°C , di 1 mole di vapore acqueo? La capacità termica dell'acqua è di circa $18 \text{ cal grado}^{-1} \text{ mole}^{-1}$, o $75 \text{ J grado}^{-1} \text{ mole}^{-1}$.
Risp. 49°C .

- 10 Alla velocità del suono nell'aria vengono assegnati i seguenti valori.

temp. ($^\circ \text{C}$)	20	100	500	1000
velocità in sec^{-1}	344	386	553	700

Confrontate questi valori con le radici quadrate della velocità quadratiche medie delle molecole di N_2 a queste temperature.

- 11 Usando il valore di d della Tab. 2.2. per argon, calcolate il libero cammino medio, il numero medio di urti che la molecola subisce in un secondo e il numero medio di urti, per metro cubo e per secondo, per le molecole di argon a 0°C e 1 atm di pressione. Quali valori si dovrebbero ottenere a 1000°C e 1 atm? Quali valori a 0°C e 100 atm?
- 12 Ricavate un'espressione del libero cammino medio per ciascun gas in funzione del diametro di collisione, della temperatura e della pressione. Preparate un grafico conveniente che mostri la variazione del libero cammino medio con la pressione, in un campo di pressioni fra 10^{-9} e 1 atm, quando il gas è l'azoto.
- 13 Usando l'Eq. [33] per la velocità media di un gas, ricavate le espressioni per i numeri di collisione Z_1 e Z_{11} , come funzioni di d , M , P , e T . Per il campo di pressione fra 10^{-9} e 1 atm, mostrate graficamente come variano Z_1 e Z_{11} con la pressione, per N_2 a 0°C .
- 14 Il rapporto fra il numero di molecole con velocità tre volte la velocità media \bar{u} e il numero di molecole con velocità media è un indice del numero di molecole veloci presenti.
a) Calcolate tale rapporto per un gas a 25°C .
b) Calcolate il rapporto del numero di molecole con velocità $3\bar{u}_{25^\circ \text{C}}$ rispetto al numero con $\bar{u}_{25^\circ \text{C}}$ per un gas a 40°C . Notate da questo calcolo come un piccolo aumento di temperatura abbia un grande effetto sul numero di molecole veloci.
Risp. $3,46 \times 10^{-4}$.
- 15 Ponete in diagramma le curve di popolazione unidimensionale e tridimensionale delle molecole, in funzione della velocità per l'idrogeno a 0°C .
- 16 Cercate di ottenere un'espressione per la distribuzione delle molecole di un gas mediante la componente lungo l'asse delle energie traslazionali, cioè ottenete un'espressione per $\frac{1}{N} \frac{dN}{d\epsilon_x}$. (Fate uso della relazione: $\frac{dN}{d\epsilon_x} = \frac{dN}{du_x} \frac{du_x}{d\epsilon_x}$.)
- 17 Mediante mezzi grafici mostrate che la funzione di popolazione-energia del problema 16 è in accordo con un'energia traslazionale media di $\frac{1}{2} kT$ per grado di libertà.
- 18 Dall'espressione di distribuzione unidimensionale del problema 16, determinate, per integrazione, l'energia cinetica media per il moto unidimensionale di una molecola.
- 19 Ripetete la distribuzione e le deduzioni di valor medio del problema 16, ma per il totale delle energie traslazionali delle molecole che si muovono in fase gassosa nello spazio tridimensionale.
- 20 Verificate, dalle espressioni di distribuzione, che la velocità più probabile per una molecola che si muove in una dimensione è nulla ed è data dall'Eq. [34] e [35].

- 21 Verificate che l'integrazione porta alla velocità media data dall'Eq. [36] (confrontate con i valori definiti in Appendice 1).

- 22 Cercate di ottenere un'espressione della velocità di perdita di massa, per effetto dell'effusione di un campione di gas attraverso un orifizio.
- 23 Quale espressione otterrete per il prodotto PV , se lo calcolate dal prodotto del numero di urti medi per unità di superficie, che si ricava dall'equazione dell'effusione del paragrafo 2.7., e dalla media delle variazioni di quantità di moto per urto, che si ricava dalla componente media della velocità nella direzione delle x , di quel paragrafo. Spiegate perché questo risultato devia, cioè se è più piccolo o più grande e in quale modo si possa ottenere il giusto risultato.
- 24 Nello studio dell'effetto di un catalizzatore solido su una reazione in fase gassosa, una miscela di gas a 25°C e a una pressione totale di 10^{-8} atm fu esposta al contatto catalitico per 15 minuti. Quante molecole e quante moli della miscela di gas vengono in contatto con un'area superficiale di 10^{-4} m^2 del catalizzatore durante questo tempo di reazione? (Ignorate il fatto che le stesse molecole possano dar luogo a urti ripetuti).
- 25 Quanto tempo è necessario a 1 mole di (a) idrogeno e (b) xenon per uscire, per effusione, nel vuoto attraverso un orifizio di 10^{-6} m^2 di diametro, se la pressione e la temperatura dei gas sono 10^{-3} atm e 0°C ?
- 26 Calcolate la frazione di molecole di elio che hanno velocità superiore, abbastanza grande per sfuggire dalla terra: (a) per una temperatura di 230 K ; che è la temperatura media a un'altezza di circa 100 km, e (b) per una temperatura di 2000 K , che si ha di giorno nella termosfera. (La velocità di fuga della terra è $1,12 \times 10^4 \text{ m s}^{-1}$).
- 27 Confrontate il volume di 20 g di H_2O a 100°C e 0,50 atm di pressione che si ottiene dalla legge del gas ideale con quello si ottiene dall'equazione di van der Waals.
- 28 Mostrate che a pressioni abbastanza basse, dove $PV = nRT$ può essere inserito nel termine di correzione della van der Waals, l'equazione di van der Waals riferita a 1 mole si riduce a:

$$PV = RT(1 + BP)$$

dove:

$$B = \frac{b}{RT} - \frac{a}{(RT)^2}$$

Usate questa approssimazione per calcolare il coefficiente viriale a 200°C dalle costanti di van der Waals per CH_4 . Confrontate con i valori dati nel problema 23 del Capitolo 1.
Risp. $B = -0,00211 \text{ atm}^{-1}$.

- 29 I gas reali mostrano delle deviazioni dal comportamento ideale, come viene suggerito dalle Figg. 1.8. e 1.9., in cui si vede che le curve PV in funzione di P partono all'inizio sia sopra che sotto la linea del gas ideale. Per ogni gas c'è una temperatura, nota come temperatura di Boyle in cui la curva diventa tangente alla linea del gas ideale. Deducete, dall'equazione di van der Waals, un'espressione per la temperatura di Boyle. Confrontate i valori calcolati della temperatura di Boyle con la forma delle curve di Fig. 1.9.
- 30 Il fattore di compressibilità di molti gas, ai loro punti critici, è approssimativamente lo stesso, e un valore medio è 0,28. In quale modo l'equazione di van der Waals si allinea con questo risultato empirico e in che misura se ne discosta?

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CHAPTER 1

The Atomic View
of Matter

1-1 INTRODUCTION

Atomic Physics is a relatively young science, having been developed mostly in this century. However, the idea that matter is built up of atoms (particles) is a very old one. The Greek philosopher Democritus (c. 460-370 B.C.), for example, theorized that not only matter but also the human soul consists of particles. Democritus had one very essential characteristic needed by every student of science, the inquisitive mind. He lacked the scientific method (Galileo Galilei, 1564-1642) and, of course, the technology needed to get any further.

Because atomic physics deals with objects (atoms) and events that are not *directly* observable with man's senses, its development often leads along paths which run counter to common sense. As we consider things and events that are orders of magnitude removed from everyday experience, the difficulty of understanding their nature increases. Our common sense enables us to understand the relationship between a brick and a house. Conceiving of the earth as round may involve a little uncommon sense, but for most people it presents no great difficulty. However, the relationship between water and a water molecule is more difficult. While we can see the earth, whether flat or round, we cannot see a water molecule even with the best of instruments. All of our information about single water molecules is of an indirect kind, yet it is a very unsophisticated chemist for whom the concept of a single water molecule is not a part of his common sense. As a man's knowledge expands, more and more facts assume the aspect of "common sense." Certain velocity relationships are common sense. To an observer in a moving car, the velocity of another moving car appears different than to an observer standing beside the highway. In fact, a very young child once observed when the car in which he was traveling was passed by another, "We are backing up from the car ahead." However, the statement made by Albert Einstein that the velocity of light is the same for all observers regardless of their own velocities is initially very uncommon sense.

In Appendix 3 we attempt to show that his statement is reasonable and can appropriately be incorporated into our common sense. The conflict between the earth's actual roundness and its apparent flatness is resolved conceptually, i.e., by imaginative understanding, with the realization that the earth is a very big sphere. Somewhat similarly, the apparent conflict between our statements about relative velocities is resolved conceptually with the realization that the velocity of light is a very large velocity. Democritus, who could propose an atomic theory in about 400 B.C., would have the courage and imagination to face the ideas that lie before us.

It is the business of philosophers to discuss the nature of reality. It is the business of physicists (once called natural philosophers) to discuss the nature of physical reality. Philosophy, therefore, includes all of physics and a lot more besides. It is natural, then, that physics should have a continuing influence on philosophy. As physical discovery is quickly put into engineering practice and made to bear on man's physical environment, so it also affects the formulation of philosophical theory and bears directly on man's outlook and interpretation of life.

The old or classical physics of Newton was extraordinarily successful in dealing with events observed in his day. Using methods he developed, it is simple to equate the earth's gravitational force on the moon to the centripetal force and obtain verifiable relationships about the behavior of the moon. The same methods can be extended to orbits which cannot be regarded as circular. In fact, three observations of a new comet enable astronomers to foretell with great accuracy the entire future behavior of the comet. Given a certain amount of specific data known as initial or boundary conditions, classical Newtonian mechanics enables us to determine future events in a large number of situations. It is easy to move a step further and argue that what Newton has demonstrated to be true often, is true always, and that given sufficient initial data and boundary conditions, laws may be found which show every future event to be determined. The motion of a falling leaf or the fluctuations in the price of peaches may be very complex phenomena. It may require tremendous amounts of data and the application of very complicated laws which we do not yet understand to be able to make predictions in these cases. The important philosophical consequence of classical mechanics was not that every problem had been solved, but that a point of view had been established. It was felt that each new discovery would fall into the Newtonian mechanistic framework. Philosophical questions like the following became more pressing. Do we humans make decisions which alter the course of our lives or are we, like the bodies of the solar system, acting according to a set of inflexible laws and in accordance with a set of boundary conditions? Are we free or is our apparent ability to make decisions an illusion? Is everything we do beyond our responsibility, having been determined at the time of creation? Although mechanistic philosophy is rather repulsive when applied to ourselves, we nevertheless lean heavily upon it in interpreting things

that go on about us. Indeed, the whole argument over whether human behavior is influenced more by heredity or environment is based on the assumption that human behavior is determined by some combination of the two.

To the extent that this mechanistic philosophy is based on classical physics, it is due for revision. Upon examination of events that are either very large or very small, we find that classical physics begins to fail. When a new theory or a modified theory has had to be applied in order to describe experimental observations, it has often resulted that the new theory is very different from classical physics. The method of attack, the mathematical techniques, and the form of the solution are often quite different. At one point we shall show that the observations of natural phenomena are inherently *uncertain*. It becomes evident, then, that if some circumstance had led to the development of atomic physics before classical physics, the influence of atomic physics on philosophy would have been against mechanism rather than for it.

Atomic physics has given us electronics and all that that word implies, including radio, radar, television, computers, etc. Atomic physics has given us nuclear energy. The new physics is as successful with submicroscopic events as classical physics was with large-scale events. But it may be that the most important benefits that can result from the study of atomic physics are philosophical rather than technical.

1-2 CHEMICAL EVIDENCE FOR THE ATOMIC VIEW OF MATTER

The speculations of Democritus and of the Epicurean school, whose philosophy was based on atomism, were not the generally accepted views of matter during the Middle Ages and the Renaissance. The prevailing concepts were those of Aristotle and the Stoic philosophers, who held that space, matter, and so on were continuous, and that all matter was one primordial stuff which was the habitat of four elementary principles—hotness, coldness, dryness, and wetness. Different materials differed in the degree of content of these principles. The hope of changing the amount of these principles in the various kinds of matter was the basis of alchemy. Not until the development of quantitative chemistry in the last half of the eighteenth century did the experimental evidence needed for evaluating the conflicting speculations about the constitution of matter begin to appear.

Antoine Lavoisier of France was outstanding among the early chemists. He evolved the present concept of a chemical element as "the last point which analysis is capable of reaching"; and he concluded from his observations on combustion that matter was conserved in chemical reactions.

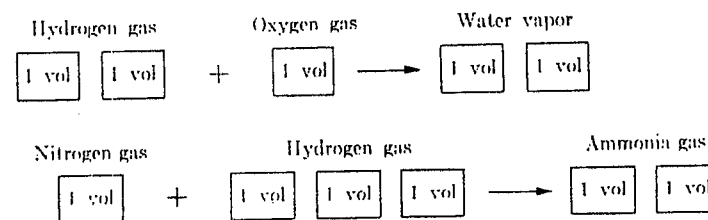
In 1799 the French chemist J. L. Proust stated the law of definite or constant proportions, which summed up the results of his studies of the substances formed when pairs of elements are combined. The law is: in every sample of any compound substance, formed or decomposed, the proportions by weight of the

constituent elements are always the same. This statement actually defines chemical compounds, because it differentiates them from solutions, alloys, and other materials which do not have definite composition.

The principal credit for founding the modern atomic theory of matter goes to John Dalton, a teacher in Manchester, England. His concern with atoms seems to have originated with his speculations about the solubilities of gases in water and with his interest in meteorology, which led him to try to explain the fact that the atmosphere is a homogeneous mixture of gases. Eventually, he believed that an element is composed of atoms that are both *physically* and *chemically* identical, and that the atoms of different elements differ from one another. In a paper he read at a meeting of the Manchester Literary and Philosophical Society in 1803. Dalton gave the first indication of the quantitative aspect of his atomic theory. He said, "An enquiry into the relative weights of the ultimate particles of bodies is a subject, as far as I know, entirely new: I have lately been prosecuting this enquiry with remarkable success." This was followed by his work on the composition of such gases as methane (CH_4), ethylene (C_2H_4), carbon monoxide (CO), carbon dioxide (CO_2), and others which led him to propose the law of multiple proportions in 1804. This law states: if substance A combines with substance B in two or more ways, forming substances C and D, then if mass A is held constant, the masses of B in the various products will be related in proportions which are the ratios of small integers. The only plausible interpretation of this law is that when elementary substances combine, they do so as discrete entities or atoms. Dalton emphasized the importance of relative masses of atoms to serve as a guide in obtaining the composition of other substances, and stressed that a chemical symbol means not only the element but also a fixed mass of that element. The introduction of the concept of atomic masses* was Dalton's greatest contribution to the theory of chemistry, because it gave a precise quantitative basis to the older vague idea of atoms. This concept directed the attention of quantitative chemistry to the determination of the relative masses of atoms.

An important law pertaining to volumes of gases was announced by Gay-Lussac in 1808. He said that if gas A combines with gas B to form gas C, all at the same temperature and pressure, then the ratios of the volumes of A, B, and C will all be ratios of simple integers. Two examples of this law are (a) the combining of two volumes of hydrogen and one volume of oxygen to form two volumes of water vapor, and (b) the union of one volume of nitrogen and three volumes of hydrogen to produce two volumes of ammonia. The following are symbolic forms of these reactions:

* It has been customary, particularly among chemists, to talk about atomic *weights*. This may be because chemists can determine relative atomic masses by weighing macroscopic samples of matter. To a physicist, the *mass* of an atom is much more meaningful than the weight. In these days of space travel, weightlessness is commonplace, but a substance never loses its mass.



It is obvious that Gay-Lussac's law, like the law of multiple proportions, implies that the substances which participate in these reactions participate in discrete or corpuscular amounts. The ratio between the number of shoes worn to the number of people wearing them is almost an exact integer, namely two, showing that both people and shoes are discrete entities. The ratio of the number of tomatoes used per serving of tomato soup is quite a different kind of situation, and if the ratio is integral it is only by coincidence.

Gay-Lussac's law supported the work of Dalton, but it also raised difficult questions about the composition of an element in the gaseous state. In the case of the first reaction given, does each atom in the given oxygen gas divide to spread through the two volumes of water vapor? If so, the indivisibility of atoms must be abandoned. Or does each entity in the oxygen gas consist of a multiplicity of atoms? If so, how many atoms are grouped together? Similar questions can be raised about each of the gases in the two reactions given. It is evident that the numerical values of the relative masses of the atoms determined from these reactions will depend upon the answers to these questions.

In 1811, Avogadro, an Italian physicist, proposed the existence of different orders of small particles for the purpose of correlating the works of Dalton and Gay-Lussac. He postulated the existence of "elementary molecules" (atoms) as the smallest particles that can combine to form compounds, and the existence of "constituent molecules" (molecules of an element) and "integral molecules" (molecules of a compound) as the smallest particles of a body that can exist in the free state. He went on to state (without proof) a very important generalization, known as Avogadro's law, that at the same temperature and pressure equal volumes of all gases contain the same number of molecules. From this law and his concepts of atoms and molecules, Avogadro showed that the ammonia-producing reaction required that nitrogen gas consist of diatomic molecules and that oxygen must also be diatomic to account for the water-vapor reaction. He further concluded that water must consist of a union of two atoms of hydrogen and one atom of oxygen.

Unfortunately, the ideas advocated by Avogadro received little notice even when revived by Ampere in 1814. The notion that hydrogen and other gases were composed of diatomic molecules was ridiculed by Dalton and others, who would not conceive of a combination of atoms of the same kind. They asked, "If two hydrogen atoms in a container filled with this gas can cling together.

why do not all cling together and condense to a liquid?" This is indeed a very good question. Science was not able to give a satisfactory answer until over a century later. (See the discussion of the covalent bond in Section 11-2.)

In the next two sections in this chapter we will describe some of the methods which were and still are used to determine the relative masses of atoms. The results obtained by the analytical chemists using these several methods during the first half of the nineteenth century were often contradictory. They frequently obtained different values for the atomic mass of the same element. By the 1850's inconsistencies were so numerous that many felt that the atomic theory of matter would have to be discarded. However, the contradictions were resolved in 1858 by the Italian chemist Cannizzaro, who had an intimate knowledge of the then known methods for determining atomic masses and a broad grasp of the whole field of chemistry. He showed that Avogadro really had provided a rational basis for finding atomic masses, and that the inconsistent results obtained by various experimenters resulted from a lack of clear distinction between atomic masses, equivalent masses, and molecular masses. The views of Cannizzaro received the approval of the scientific world when they were adopted by the international conference on atomic masses which met in Karlsruhe, Germany, in 1869. This, then, is the year in which the fundamental ideas of modern chemistry were widely accepted.

1-3 MOLECULAR MASSES

After Cannizzaro had clarified and established some of the basic definitions in chemistry, Avogadro's law opened the door to one of the methods for determining molecular masses. No one had any idea of what the mass of a single molecule was, but once there was a way of isolating equal numbers of different kinds of molecules, the relative masses could be determined. The hydrogen molecule was found to be the lightest molecule, and the hydrogen atom proved to be the lightest atom. In 1815 Proust had proposed that the relative atomic mass of hydrogen be arbitrarily taken as one. On this basis most other light atoms and molecules had relative masses which were nearly integers. But, for reasons to be discussed later, it turned out that the atomic masses of many of the heavier atoms were not very nearly integers. Hydrogen appeared to be a poor basis for the system, and more nearly integral atomic masses for all atoms could be obtained by making a heavier atom the basis of the system.

For many years physicists and chemists used two different systems, both based on the mass of oxygen. On the physics scale the mass of the isotope (Section 2-7) of oxygen having 8 protons and 8 neutrons in the nucleus was set at 16. On the chemistry scale the natural mixture of oxygen isotopes was given an average mass value of 16. In 1961 the two scales were replaced by a common atomic-mass scale in which the mass of the carbon isotope ^{12}C (6 protons and

6 neutrons) is set to 12. On this scale, the atomic mass of hydrogen is not exactly unity, although it is nearly so.

These relative molecular and atomic masses are all dimensionless ratios. If about four parts by weight of hydrogen were combined with 32 parts by weight of oxygen, about 36 parts by weight of water vapor can be formed, according to the familiar equation, $2\text{H}_2 + \text{O}_2 = 2\text{H}_2\text{O}$.

Chemists as well as physicists measure amounts of material in grams or in moles. A mole is defined as the amount of a given substance containing the same number of molecules as the number of atoms in 12 grams of ^{12}C . One mole of ^{12}C is 12 grams, one mole of carbon in its natural mixture of isotopes is 12.01115 grams, one mole of H_2O is 18.0153 grams, etc. The number of atoms in 12 grams of ^{12}C (number of molecules in a mole) is called Avogadro's number or the Avogadro constant, N_A , and it is of basic importance in physics and physical chemistry. (Note that the mole and the Avogadro constant have been defined in terms of 12 grams of ^{12}C . This is the modern practice. However, these definitions do not always conform to the MKSA system of units.* Therefore, we will on occasion use the kilomole, kmole, which is 1000 moles. Obviously a kilomole of carbon 12 has a mass of 12 kilograms.)

The value of the Avogadro constant was of relatively minor importance to chemistry in the early nineteenth century and its magnitude was not even estimated until Loschmidt did so in 1865. We will discuss Perrin's method of determining it later in this chapter. Here is an interesting case where knowing the existence of a number was more important than knowing its magnitude as, for example, in determining the relative masses of the atoms involved in the ammonia-producing hydrogen-nitrogen reaction previously described. The value of the Avogadro constant is by modern measurements

$$N_A = (6.02217 \pm 0.00004) \times 10^{23}$$

particles per mole. Only after the magnitude of the Avogadro constant was known could the absolute mass of an atomic particle be computed. Since N_A ^{12}C atoms of 12 u (mass units) is 12 grams, the mass (in grams) of one unit is clearly

$$1 \text{ u} = 1/N_A = (1.66054 \pm 0.00001) \times 10^{-24} \text{ g.}$$

It follows from Avogadro's law that the volume of a mole of a gas is the same for all gases. The normal volume of a perfect gas or the standard molar

* For students not familiar with the MKSA system, a brief review is given in Appendix 1.

volume of an ideal gas, V_0 , is the volume occupied by a mole of the gas at a pressure of 1 standard atmosphere and a temperature of 0°C . The value of V_0 is

$$(2.24136 + 0.00030) \times 10^{-2} \text{ m}^3 \text{ per mole. } (22.4 \text{ l})$$

1-4 ATOMIC MASSES

Avogadro's law provided a systematic method for determining molecular masses, but a large amount of quantitative data on the formation of various compounds were required before the atomic masses of the known elements could be determined. The situation is somewhat like the following: Suppose that man *A* pays man *B* \$1.00 in coin, using no coin smaller than quarters, and that we wish to determine how this is done. He may do this in any one of four ways:

- one \$1.00 coin,
- two 50¢ coins,
- one 50¢ and two 25¢ coins,
- four 25¢ coins.

If man *B* now pays man *C* 25¢, possibilities (a) and (b) are eliminated, but there is still a doubt as to how the original transaction was made. By careful observation of further transactions of those who spend the original \$1.00, it could be determined just what coins *A* must have had originally.

An aid to the solution of this puzzle was the empirical discovery by Dulong and Petit, in 1819, that for most elements in the solid state the specific heat per mole at constant volume is about $6 \text{ cal} \cdot \text{mole}^{-1} \cdot ^\circ\text{K}^{-1}$. The law of Dulong and Petit permits a rough independent determination of atomic masses by dividing this constant by the specific heat measured in calories per gram. We shall discuss the theoretical basis of this law in Section 3-15.

The masses of atoms are now measured on the ^{12}C scale in mass spectrometers with an almost fantastic precision. (Uncertainties of about one part per million are not uncommon.) See Section 2-8.

* If it seems strange that this and some other constants are given with the uncertainty expressed to more than one significant figure, refer to the article, "Probable Values of the General Physical Constants," by R. T. Birge, [*Phys. Rev. Suppl.* 1 (1929), p. 6]. We note here only that the concepts of probable errors and significant figures do not correspond completely. If the probable error can be determined to less than 10 percent of itself, then more than one significant figure is required to express it.

Principal articles containing the values of various constants are: "Values for the Physical Constants Recommended by NAS-NRC," *Nat. Bur. Std. (U.S.) Tech. News Bull.* 47 (1963), p. 175; "World Sets Atomic Definition of Time," *Nat. Bur. Std. (U.S.) Tech. News Bull.* 48 (1964), p. 209; Mechtly, E. A., *The International System of Units*, NASA SP-7012. Washington, D.C.: U.S. Government Printing Office (1964); Cohen, E. R. and J. W. M. Du Mond, "Our Knowledge of the Fundamental Constants of Physics and Chemistry in 1965," *Rev. Mod. Phys.* 37 (1965), p. 537.

1-5 PERIODIC TABLE

Probably the most significant discovery in all chemistry, aside from the atomic nature of matter, was the periodic properties of the elements, now depicted in the familiar periodic table of the elements (*Appendix 2*). The chemical properties of this table are probably familiar to most readers of this book: the physical properties will be discussed later. The table was proposed independently by Meyer and by Mendelée'v in 1869. Its usefulness lay both in its regularities and in its irregularities. One interesting irregularity in the original table was that in order to have the elements fall in positions consistent with their chemical properties, it was necessary to leave numerous spaces unoccupied. Mendelée'v suggested that these spaces would be filled with as yet undiscovered elements. Using his table, he was able to describe in considerable detail the properties these elements could be expected to have when they were discovered. It was nearly one hundred years before all the predictions that Mendelée'v made were fulfilled.

Reflect, for a moment, on the vast simplification that the chemical discoveries here outlined provide. Looking about us, we see innumerable kinds of materials. The atomic view indicates that these materials are of discrete kinds whose number, however large, is not uncountable. The discovery of elements is a further simplification in that the many materials we encounter are shown to be composed of only about one hundred chemically distinguishable materials, many of which are rare. It turns out that even these elements are not a heterogeneous group but are subject to further classification into a periodic table. The problems of chemistry are many; however, it is easy to see that things are much simpler than might at first appear.

1-6 PHYSICAL EVIDENCE FOR THE ATOMIC VIEW OF MATTER

In our discussion thus far, all atomic properties have been inferred from studies of gross matter. In 1827 the English botanist Robert Brown observed that microscopic pollen grains suspended in water appear to dance about in random fashion. At first the phenomenon was ascribed to the motions of living matter. In time, however, it was found that any kind of fine particles suspended in a liquid performed such a perpetual dance. Eventually it was realized that the molecules of a liquid are in constant motion and that the suspended particles recoiled (Brownian movement), when hit by the molecules of the liquid. However, long before the equations for Brownian movement were derived early in the twentieth century, the particles of matter were thought of as moving about in a random manner and undergoing frequent collisions. Such processes are decidedly in the domain of physics. How can the principles of mechanics be applied to molecular collisions?

The simplest state of matter to consider was a gas. The ideal gas law, for n moles of a gas is $pV = nRT$, where R is the universal gas constant per mole

and p , V , and T are the pressure, volume, and temperature, respectively. This law was a well-established empirical relationship, and its derivation was one of the objectives of physics. The application of classical physics to the mechanics of gases is called the kinetic theory of gases. Although Daniel Bernoulli had some success in developing this theory as early as 1738, the principal contributions that led to its establishment were made between 1850 and 1900 by Clausius, Maxwell, Boltzmann, and Gibbs.

1-7 KINETIC THEORY OF GASES; MOLAR HEAT CAPACITY

Early in our study of physics, we investigated the mechanics of bodies that can be regarded as particles. The study of extended bodies was treated by introducing certain averages, and the translational problem of extended bodies was solved by introducing the concept of a center of mass that moves as though it were a particle. The study of rotational properties of extended bodies was similarly facilitated by the introduction of another average property of the body, its moment of inertia. In the kinetic theory of gases, we assume that pressure, volume, temperature, etc., are averages of properties of all the molecules of a gas. Kinetic theory is a large and elegant subject. We can convey its spirit by deriving the ideal gas law and a few other relationships.

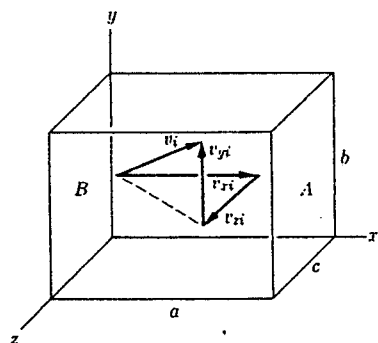


Fig. 1-1 Container with gas of N particles.

Consider a rectangular container, the edges of which are parallel to the x -, y -, and z -axes and have dimensions a , b , and c , as shown in Fig. 1-1. There are N identical particles, each of mass m , in the box moving in random directions with a wide range of speeds. These identical particles may be, but are not necessarily, atoms or molecules.

We assume that the particles are very small so collisions between them are rare compared to collisions with the plane walls of the container. Neglecting minor forces such as gravity and intermolecular forces, we shall consider that the only forces acting on the particle are those resulting from collisions with the

walls. We number the particles $1, 2, \dots, i, \dots, N$. Figure 1-1 shows the i th particle, whose velocity is v_i . This velocity may be broken into the rectangular components v_{xi} , v_{yi} , and v_{zi} , as shown. We assume collisions to be perfectly elastic such that when a particle strikes a wall the velocity component related to the axis that is perpendicular to that wall is reversed in direction but unchanged in magnitude. The other two velocity components remain unchanged. Thus if the particle strikes side A , the x -component of its momentum is changed from $+mv_{xi}$ to $-mv_{xi}$. The net change in the x -component of its momentum is

$$(-mv_{xi}) - (+mv_{xi}) = -2mv_{xi}.$$

Since collision with the wall causes the particle to change its momentum, the wall experiences an impulsive force. This impulsive force is unknown because we cannot estimate the time of contact in a meaningful way. Fortunately, it is not the impulsive force but the average force from repeated hits that we seek. Since collisions with the top, bottom, far, and near sides have no effect on v_{xi} , and since collisions with ends A and B merely reverse the direction of v_{xi} , we see that the time interval between successive hits on side A is the total x -distance, $2a$, divided by the x -component of the velocity or $2a/v_{xi}$. By applying Newton's second law, we find the average force F_i of the wall on the i th particle to be

$$F_i = \frac{\Delta(mv)}{\Delta t} = \frac{-2mv_{xi}}{2a/v_{xi}} = -\frac{mv_{xi}^2}{a}. \quad (1-1)$$

This force is equal in magnitude and opposite in direction to the force of the particle on the wall and thus the particle produces an average pressure on side A given by

$$p_i = \frac{-F_i}{\text{area}} = \frac{-F_i}{bc} = \frac{mv_{xi}^2}{abc} = \frac{mv_{xi}^2}{V}, \quad (1-2)$$

where V is the volume of the container.

The pressure we have computed is due to but one, the i th, particle. The pressure from each particle is computed the same way. Adding the pressures from the N identical particles, we have

$$p = \sum_{i=1}^N p_i = \frac{m}{V} \sum_{i=1}^N v_{xi}^2. \quad (1-3)$$

To evaluate the sum on the right-hand side of the equation we note (see Fig. 1-1) that

$$v_i^2 = v_{xi}^2 + v_{yi}^2 + v_{zi}^2. \quad (1-4)$$

Since this equation holds for each of the particles, we can add the corresponding equations and obtain

$$\sum_{i=1}^N v_i^2 = \sum_{i=1}^N v_{xi}^2 + \sum_{i=1}^N v_{yi}^2 + \sum_{i=1}^N v_{zi}^2. \quad (1-5)$$

We now define the mean square velocity, \bar{v}^2 , to be the average of the sum of the squares of the velocities; therefore

$$\bar{v}^2 = \left(\sum_{i=1}^N v_i^2 \right) / N. \quad (1-6)$$

Applying this definition to all terms in Eq. (1-5), we find that it becomes

$$\bar{v}^2 = \bar{v}_x^2 + \bar{v}_y^2 + \bar{v}_z^2, \quad (1-7)$$

and, substituting terms from Eq. (1-6) into Eq. (1-3), we get

$$p = \frac{m}{V} N \bar{v}_x^2. \quad (1-8)$$

Since we assume these velocities to be completely random in direction and magnitude, the three mean square velocity components must be equal or $\bar{v}_x^2 = \bar{v}_y^2 = \bar{v}_z^2$. This assumption enables us to deduce from Eq. (1-7) that

$$\bar{v}^2 = 3\bar{v}_x^2 = 3\bar{v}_y^2 = 3\bar{v}_z^2. \quad (1-9)$$

The square root of the quantity \bar{v}^2 is called the root-mean-square speed, or velocity, v_{rms} . Substituting \bar{v}_x^2 from Eq. (1-9) into Eq. (1-8), we get

$$p = \frac{Nm}{V} \frac{\bar{v}^2}{3}.$$

or

$$pV = \frac{1}{3} Nm \bar{v}^2. \quad (1-10)$$

When the particles in the container are the molecules of a gas, then the number of moles n of the gas in the container equals the total number of molecules N in it divided by the number of molecules in a mole N_A , the Avogadro constant. Therefore we have $n = N/N_A$ or $N = nN_A$. Since the product of the mass of a molecule and the Avogadro constant is the molecular mass M , we can express the total mass of the gas in the box as $Nm = nN_A m = nM$. When this result is substituted in Eq. (1-10) it becomes

$$pV = \frac{1}{3} nM \bar{v}^2. \quad (1-11)$$

This is not the result we sought, $pV = nRT$, so we have as yet no justification for the many assumptions we have made. The result is interesting, however, because it contains the pV term, and the term $\frac{1}{3} nM \bar{v}^2$ has a familiar look. If we write

$$\frac{1}{3} nM \bar{v}^2 = \frac{2}{3} \left(\frac{1}{2} nM \bar{v}^2 \right), \quad (1-12)$$

the quantity in parentheses is clearly the total translational kinetic energy of the molecules. This energy is the total internal energy of the gas U if the molecules do not have rotational energy and if it can be assumed that no forces

of attraction or repulsion exist which could give rise to molecular potential energy (real gas). By combining Eqs. (1-11) and (1-12), we obtain

$$pV = \frac{2}{3} U. \quad (1-13)$$

We compare this result with the ideal-gas law $pV = nRT$ and find that our calculations suggest

$$U = \frac{3}{2} nRT \quad (1-14)$$

for an ideal gas; that is, the temperature is a measure of the internal energy of the gas.* Let us now see how this result compares with measurements on real gases.

When a gas is heated at constant volume, the heat energy supplied causes a temperature change that must increase the energy of the gas since no work is done. The change in internal energy with respect to temperature is given by

$$dU/dT = \frac{3}{2} nR. \quad (1-15)$$

The change in internal energy with respect to temperature of one mole of an ideal gas at constant volume is called the molar heat capacity C_v . Therefore we obtain

$$C_v = \frac{3}{2} R, \quad \times 1 \text{ mole} \quad (1-16)$$

and its value is

$$C_v = \frac{3}{2} R = \frac{3}{2} \times \frac{8.31 \text{ J}}{\text{mole} \cdot ^\circ\text{K}} \times \frac{1 \text{ cal}}{4.18 \text{ J}} = 2.97 \text{ cal} \cdot \text{mole}^{-1} \cdot ^\circ\text{K}^{-1}.$$

The experimental values of C_v for several gases at room temperature are given in Table 1-1. Note that three values agree very closely with the computed value but that the others are quite different. Both the agreements and the disagreements are interesting. The values which agree are those of monatomic gases, which come closest to the ideal gas. We shall have more to say about the apparent disagreements. The point here is to recall that in our discussion of kinetic theory we assumed that our molecules were isolated elastic spheres. Our result apparently does not apply to diatomic dumbbells or to more complicated molecules.

* Temperature can be defined by the aid of a constant-volume gas thermometer as being proportional to the pressure (from $pV = nRT$). This approach assumes that the medium is an ideal gas which, strictly speaking, does not exist, although some gases come close to it. A more satisfactory definition of temperature was given by Lord Kelvin in 1848. It is based on the heat transfers in the isothermic parts of the cycle of a Carnot engine and is independent of the working substance. (For example, see U. Ingard and W. L. Kraushaar, *Mechanics, Matter, and Waves*. Reading, Mass.: Addison-Wesley, 1960, p. 534.)

Table 1-1 C_v of gases

Gas		C_v , cal·mole ⁻¹ ·°K ⁻¹
Helium,	He	3.00
Argon,	A	3.00
Mercury,	Hg	3.00
Hydrogen,	H ₂	4.82
Oxygen,	O ₂	4.97
Chlorine,	Cl ₂	6.01
Ether,	(C ₂ H ₅) ₂ O	30.8

1-8 EQUIPARTITION OF ENERGY

The agreement we have observed for monatomic molecules would not have been possible had there not been the number 3 in the expression $C_v = 3R/2$. Looking back over our derivation, we find that the 3 entered into the calculation from the statement $\bar{v}^2 = 3\bar{v}_x^2$, that is, because the molecule was free to move in three-dimensional space. The expression for the average kinetic energy of translation of the molecules of a gas is composed of three equal parts, $R/2$ per degree of absolute temperature associated with each coordinate. The principle of equipartition of energy states that if a molecule can have energy associated with several coordinates, the average energy associated with each coordinate is the same. Because of this principle, the number of coordinates necessary to specify the position and configuration of a body is called the number of its degrees of freedom.

A monatomic molecule requires three coordinates to specify its position. A rigid diatomic molecule requires three position coordinates and two more are necessary to specify its configuration. If we assume the second atom is at a fixed distance from the first, its location is specified as being on a sphere with the first atom at its center. It requires but two additional coordinates to specify where on this sphere the second atom lies. Thus the addition of a second atom adds two degrees of freedom to the molecule. If our derivation for molar heat capacity had been based on diatomic instead of monatomic molecules, we would have obtained $5R/2$ instead of $3R/2$. We find that $5R/2 = 4.95$ cal mole⁻¹·°K⁻¹, which agrees closely with the measured molar heat capacities of such diatomic molecules as hydrogen and oxygen, as shown in Table 1-1. Six coordinates are enough to specify the position of any rigid molecule, however complex, but if the molecules are composed of vibrating atoms, then the number of degrees of freedom may become very large. This accounts for the large molar heat capacity of ether. A fuller discussion of heat capacities requires the introduction of quantum theory but classical kinetic theory reveals much, both qualitatively and quantitatively.

With the help of independent data from molar-heat capacities, we have found that the kinetic theory of matter provides a quantitative mechanical model for both the ideal-gas law and molar-heat capacities. The qualitative result, Eq. (1-14), applies only for the ideal gas, as demonstrated in the subsequent discussion of specific heat. However, Eq. (1-11) has more general validity. Using $pV = nRT$, we find from Eq. (1-11) that

$$\frac{1}{2}M\bar{v}^2 = \frac{3}{2}RT. \quad (1-17)$$

Substituting for the molecular mass $M = N_A m$, where m is the mass of one molecule, we get

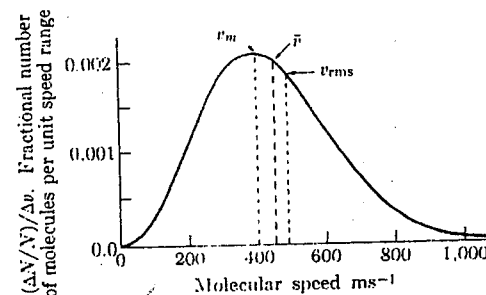
$$\frac{1}{2}m\bar{v}^2 = \frac{3}{2}(R/N_A)T = \frac{3}{2}kT. \quad (1-18)$$

The new constant $k = R/N_A$ is called Boltzmann's constant or the gas constant per molecule. Its value is $k = 1.38062 \times 10^{-23}$ J·°K⁻¹. Equation (1-18) shows that the average kinetic energy of translation of the molecules of a gas depends only on the absolute temperature. The average energy per degree of freedom is clearly $\frac{1}{2}kT$.

At a given temperature, the lighter molecules have the greater speeds. As calculated from Eq. (1-18), the root-mean-square speed of hydrogen molecules at room temperature is about 1800 m s⁻¹, or more than 1 mi s⁻¹.

1-9 MAXWELL'S SPEED DISTRIBUTION LAW

We have found that \bar{v}^2 can be computed from the temperature of a gas. The speed thus determined is one of the important average properties of a gas. But the average doesn't tell the whole story. For many physical and chemical problems, it is important to know the *speed distribution* of the molecules. For instance, we may ask how many molecules have more than twice the root-mean-square speed $v_{rms} = (\bar{v}^2)^{1/2}$ or how many have speeds in the interval $0.79 v_{rms}$ to $0.80 v_{rms}$. This can be found from Maxwell's distribution law, which we shall proceed to derive. Figure 1-2 is a plot of this distribution function as applied to N₂ gas at a temperature of $T = 273^\circ\text{K}$ (0°C).

Fig. 1-2 Distribution of speeds for nitrogen molecules at 0°C .

The derivation of Maxwell's distribution law is based on the following assumptions:

Assumption 1. Space is isotropic. Therefore the x -components of velocity exhibit the same distribution as the components along any other axis (including the negative x -axis).

Assumption 2. The distribution of x -velocities is independent of the velocity components v_y and v_z .

Assumption 3. The average energy of the molecules is given by Eq. (1-18). $\frac{1}{2} m \overline{v^2} = \frac{3}{2} kT$

We start by writing the distribution function for the x -components of velocity as

$$\Delta N(v_x) = N f(v_x^2) \Delta v_x. \quad (1-19)$$

Here $\Delta N(v_x)/N$ is the fraction of the total number of molecules N with velocity in the small interval v_x to $v_x + \Delta v_x$. This fraction, divided by Δv_x , is the distribution function f , which is written in terms of v_x^2 instead of v_x . This will simplify the following derivation and does not introduce any new restrictions on the function beyond what is included in assumption no. 1.

Further, because of assumption no. 1, we can write

$$\Delta N(v_y) = N f(v_y^2) \Delta v_y, \quad (1-20)$$

$$\Delta N(v_z) = N f(v_z^2) \Delta v_z, \quad (1-21)$$

where the function f is the same as in Eq. (1-19), but with different arguments.

By writing the distribution function for x -velocity as a function of v_x^2 only and not also of v_y^2 or v_z^2 , we have used assumption no. 2. (Other parameters, as for instance the temperature, may of course enter into the arguments of these functions.)

Figure 1-3 illustrates the velocity distribution of a sample gas. Note that the figure represents *velocity space* with coordinates v_x , v_y , and v_z , and that the *locations* of the particles (x , y , z) are not depicted. The gas can be enclosed for instance in a cubical container and in thermal equilibrium with its walls. Every time a molecule bounces off a wall, the corresponding velocity component changes sign and the corresponding point in Fig. 1-3 changes position. The overall picture, however, remains the same.

According to Eq. (1-19), the product $f(v_x^2) \Delta v_x$ can be interpreted as the probability for finding a given molecule in the velocity interval v_x to $v_x + \Delta v_x$. The probability for finding that the same molecule at the same instant of time also has y -velocity in the interval v_y to $v_y + \Delta v_y$ and z -velocity in the interval v_z to $v_z + \Delta v_z$ is clearly

$$\frac{\Delta N(v_x, v_y, v_z)}{N} = f(v_x^2) f(v_y^2) f(v_z^2) \Delta V, \quad (1-22)$$

where $\Delta V = \Delta v_x \Delta v_y \Delta v_z$.

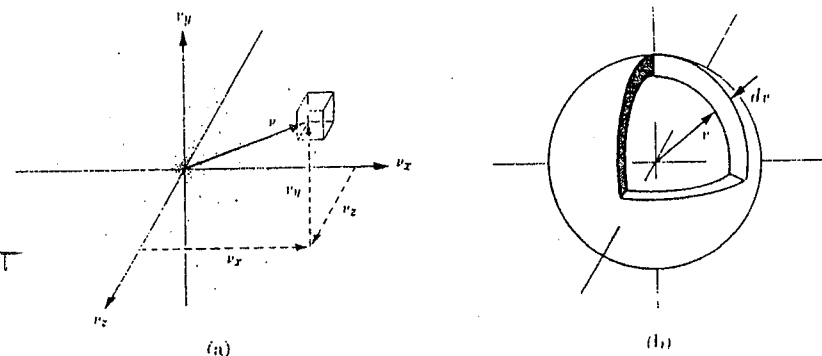


Fig. 1-3 (a) Velocity distribution of the molecules in a sample of gas. (b) Volume element in velocity space for speeds between v and $v + dv$.

The volume element in velocity space $\Delta v_x \Delta v_y \Delta v_z$ is shown in Fig. 1-3 at the tip of the velocity vector v . We now imagine a new coordinate system placed with the x -axis along v and with the new y - and z -axes perpendicular to it. In this new system, the fraction of molecules in a volume element ΔV of the same size as $\Delta v_x \Delta v_y \Delta v_z$ but oriented differently will be

$$\frac{\Delta N(v, 0, 0)}{N} = f(v^2) f(0) f(0) \Delta V. \quad (1-23)$$

In the rotated system $v_y = 0$ and $v_z = 0$ and the functions $f(0)$ can be replaced by a constant A . Since Eqs. (1-22) and (1-23) describe the same fraction expressed in two different coordinate systems, we can write

$$A^2 f(v^2) = f(v_x^2) f(v_y^2) f(v_z^2), \quad \text{equally: remember} \quad (1-24)$$

with $v^2 = v_x^2 + v_y^2 + v_z^2$.

We shall now prove that the only type of function f that satisfies Eq. (1-24) is the exponential. We denote with f' the derivative of f with respect to its argument and take the partial of (1-24) with respect to v_x . We obtain

$$A^2 f'(v^2) = f'(v_x^2) f(v_y^2) f(v_z^2).$$

Dividing by Eq. (1-24), we obtain

$$\frac{f'(v^2)}{f(v^2)} = \frac{f'(v_x^2)}{f(v_x^2)}.$$

By a similar procedure, including taking partial derivatives with respect to v_y and v_z^2 , we obtain

$$\frac{f'(v^2)}{f(v^2)} = \frac{f'(v_x^2)}{f(v_x^2)} = \frac{f'(v_y^2)}{f(v_y^2)} = \frac{f'(v_z^2)}{f(v_z^2)}. \quad (1-25)$$

Now comes an argument that is used very often in solving separable differential equations. The function $F(v_x^2) = f'(v_x^2)/f(v_x^2)$ depends only upon v_x^2 , meaning that it does not vary if v_x^2 is fixed and v_y^2 of v_z^2 varies. The only way in which Eq. (1-25) can be fulfilled for *all* possible values of v_x^2 , v_y^2 , and v_z^2 is then that each fraction is equal to the same constant (call it $-\beta$), so that

$$\frac{f'(v_x^2)}{f(v_x^2)} = \frac{1}{f} \frac{df}{dv_x^2} = -\beta.$$

The solution of this is

$$\ln f = -\beta v_x^2 + \text{const},$$

which gives

$$f = f(0)e^{-\beta v_x^2} = Ae^{-\beta v_x^2}. \quad (1-26)$$

The reason why we chose a negative real number, $-\beta$, for separation constant is now apparent. A positive number would make $f \rightarrow \infty$, which is not realistic, and an imaginary constant will give an imaginary answer, which also is non-physical.

We can now write the form of the distribution function for the x -component of velocity:

$$\frac{\Delta N(v_x)}{N} = Ae^{-\beta v_x^2} \Delta v_x, \quad (1-27)$$

where A and β remain to be determined. We postpone the determination of β and find A by imposing the obvious condition that the probability that the molecule has *some* velocity between $-\infty$ and ∞ is unity. We therefore write

$$\int_{-\infty}^{\infty} Ae^{-\beta v_x^2} dv_x = 1.$$

This procedure, which is called normalization, yields $A = (\beta/\pi)^{1/2}$. (The integral of the Gaussian function $\exp(-\beta x^2)$ can be found in any table of definite integrals.)

The velocity distribution function Eq. (1-22) combined with Eq. (1-24) gives

$$\frac{\Delta N(v_x v_y v_z)}{N} = \left(\frac{\beta}{\pi}\right)^{3/2} e^{-\beta v^2} \Delta V, \quad (1-28)$$

where we have replaced A with $(\beta/\pi)^{1/2}$. This exponential function shows that the most probable (or "fullest") volume element $\Delta V = \Delta v_x \Delta v_y \Delta v_z$ of specified velocity "size" is at the origin where $v = 0$. If we move the same velocity volume element away from the origin, fewer velocity vectors will terminate within it. One reason for this is that as we move the volume element away from the origin, we are becoming specific concerning the direction of motion of the molecules.

If we move from the distribution of *velocities* to the distribution of *speeds*, we can drop the restriction on direction of motion. Molecules with *speeds* between V and $V + \Delta V$ lie in a spherical shell in velocity space. To get the speed distribution function, we replace $\Delta V = \Delta v_x \Delta v_y \Delta v_z$ by $\Delta V = 4\pi r^2 \Delta r$, where v now means speed rather than velocity. We then find Maxwell's distribution of speeds to be

$$\frac{\Delta N(v)}{N} = 4\pi(\beta/\pi)^{3/2} v^2 e^{-\beta v^2} dv. \quad (1-29)$$

The distribution of speeds is no longer maximum at the origin. The reason is that for a given ΔV , our speed volume element at the origin is small and includes more velocity space as the speed V increases.

It remains to determine the constant β . For this purpose we use assumption no. 3 and write

$$\int_0^{\infty} (\frac{1}{2}mv^2) 4\pi(\beta/\pi)^{3/2} v^2 e^{-\beta v^2} dv = \frac{3}{2}kT.$$

Again by using a table of integrals, we find that

$$\beta = \frac{m}{2kT}. \quad (1-30)$$

Inserted into Eq. (1-29), this gives

$$\frac{\Delta N(v)}{N} = 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} v^2 e^{-mv^2/2kT} \Delta v. \quad (1-31)$$

This is Maxwell's distribution law, which is illustrated by one example in Fig. 1-2.

The most probable speed v_m and the average speed \bar{v} can be found very simply by the aid of Eq. (1-31); they are

$$v_m = \sqrt{2/3} v_{rms} = 0.817 v_{rms} \quad (1-32)$$

and

$$\bar{v} = \sqrt{8/3\pi} v_{rms} = 0.921 v_{rms}, \quad (1-33)$$

with $v_{rms} = (3kT/m)^{1/2}$ from Eq. (1-18).

Maxwell's distribution of speeds was employed to calculate other gas properties and was indirectly verified in terms of these secondary properties. A direct experimental verification was obtained by Zartman and Ko in 1930. They used an oven, shown in Fig. 1-4, containing bismuth vapor at a known high temperature (827°C). Bismuth molecules streamed from a slit in the oven into an evacuated region above.* The beam was made unidirectional by

* Fast-moving molecules escape from the oven more often than slow ones. Computation shows that if the oven is at a temperature T , the root-mean-square speed of escaping molecules is the same as the root-mean-square speed within an oven at a higher temperature, $4T/3$.

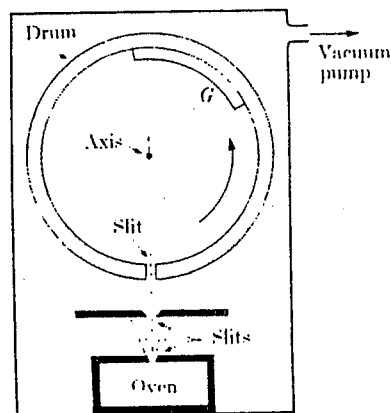


Fig. 1-4 Diagram of apparatus used by Zartman and Ko.

another slit, which admitted only properly directed molecules. Above the slit was a cylindrical drum that could be rotated in the vacuum about a horizontal axis perpendicular to the paper. A slit along one side of the drum had to be in a particular position to enable the beam of molecules to enter it. When the drum was stationed so that the beam could enter, the beam moved along a diameter of the drum and was deposited on a glass plate G mounted on the inside surface of the drum opposite the slit. During the experiment, the drum was rotated at a constant angular velocity so that short bursts of molecules were admitted on each rotation. Because the speeds of the molecules varied, some crossed the diameter quickly and others took much more time, and since the drum was turning while the molecules were moving across it, they struck the glass plate at different places. Thus the distribution of speeds was translated by the apparatus into a distribution in space around the inside of the drum, as indicated by the variation in the darkening of the glass where the bismuth was deposited. The thickness of the deposit was measured optically, and comparison of the experimental distribution of speeds with Maxwell's theoretical distribution expression showed excellent agreement.

1-10 COLLISION PROBABILITY; MEAN FREE PATH

If molecules were truly geometrical points, no collisions would take place between them. Actual molecules, however, are of finite size, and for the purposes of this discussion we are assuming that a molecule is a rigid, perfectly elastic sphere. A collision between two molecules is considered to take place whenever one molecule makes contact with another. Let us refer to one of the colliding molecules as the target molecule, of radius r_t , and to the other as the bullet molecule, of radius r_b . Then a collision occurs whenever the distance

between the centers of the molecules becomes equal to the sum of their radii, $r_t + r_b$, as in Fig. 1-5(a).

When we are considering collisions of molecules of a given gas with other molecules of the same gas, the radii r_t and r_b are equal and there is no difference between target molecules and bullet molecules. In many instances, however, we wish to consider collisions between different kinds of particles, and so we shall speak of the target molecules as though they differed from the bullet molecules.

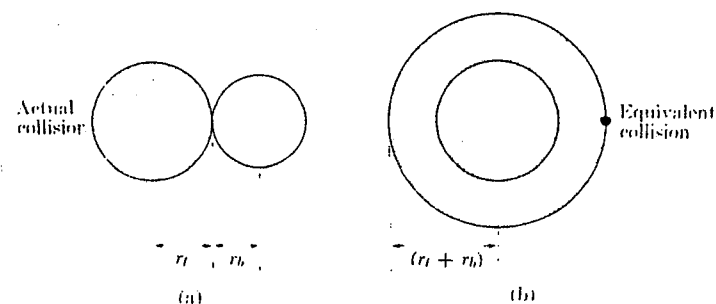


Fig. 1-5 For mathematical convenience, the actual collision depicted in part (a) may be represented by the equivalent collision shown in (b).

Since it is only the center-to-center distance that determines a collision, it does not matter whether the target is large and the bullet is small, or vice versa. We may therefore replace an actual collision with the equivalent collision shown in Fig. 1-5(b), in which the bullet molecule has been considered to shrink to a geometrical point and the target molecule to expand to a sphere of radius $r_t + r_b$.

Now consider a thin layer of material of dimensions l , l , and dx . The layer contains (equivalent) target molecules only, and to begin with we assume that these are at rest. We then imagine that a very large number N of bullet molecules are incident normally on the face of the layer like a blast of pellets from a shotgun, in such a way that they are distributed over the face. If the thickness of the layer is so small that no target molecule can hide behind another, the layer presents to the bullet molecules the appearance shown in Fig. 1-6, where the shaded circles represent the target molecules and the black dots the bullet molecules.

Most of the bullet molecules will pass through the layer, but some will collide with target molecules. The ratio of the number of collisions, dN , to the total number of bullet molecules, N , is equal to the ratio of the area presented by the target molecules to the total area presented by the layer:

$$\frac{dN}{N} = \frac{\text{target area}}{\text{total area}}$$

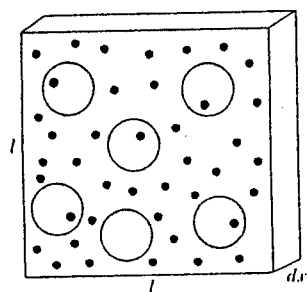


Fig. 1-6 Target with equivalent target molecules (shaded) and bullet molecules (dots).

The target area σ of a single (equivalent) molecule is

$$\sigma = \pi(r_t + r_b)^2. \quad (1-34)$$

This area is called the *collision cross section* of one (equivalent) molecule. The total target area is the product of this and the number of molecules in the layer. If there are n target molecules per unit volume, this number is $nl^2 dx$, so the total target area is

$$n\sigma l^2 dx.$$

The total area of the layer is l^2 , so

$$\frac{dN}{N} = \frac{n\sigma l^2 dx}{l^2} = n\sigma dx. \quad (1-35)$$

In the preceding equation the quantity dN/N is the fractional number of molecules that undergo collisions and therefore this ratio is simply the probability of a collision. (Strictly, this should have a negative sign because dN molecules are removed from the stream of bullets.) In the beginning of this discussion the cross section was thought of as an actual area presented by target molecule, but this was soon replaced by an equivalent area. As we shall see later in quantum mechanical systems, e.g., atoms and molecules, we cannot accept the concept of a sharp boundary as shown in Fig. 1-5. However, we can use Eq. (1-35) to define the cross section σ , which then becomes a measure of the probability for collision.

If N_0 bullet molecules per unit area are incident normally on the face of a layer of material containing stationary molecules having the macroscopic cross section $n\sigma$, then N , the number transmitted undeflected per unit area through a finite thickness x , can be found by integrating Eq. (1-35). We then have

$$\int_{N_0}^N -\frac{dN}{N} = \int_0^x n\sigma dx, \quad (1-36)$$

and obtain

$$\ln \frac{N}{N_0} = -n\sigma x$$

or

$$N = N_0 e^{-n\sigma x}. \quad (1-37)$$

This exponential equation is plotted as a solid line in Fig. 1-7.

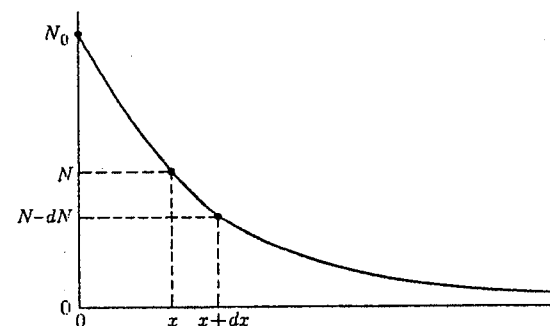


Fig. 1-7 Number of molecules N passing through a target layer undeflected versus thickness x of layer.

Let us next follow in imagination a single bullet molecule as it makes its way through a very thick target along the zigzag path shown in Fig. 1-8. We wish to obtain an expression for the average distance traveled between collisions, known as the *mean free path*, L . This can be deduced from the results above by a type of reasoning that is common and useful in problems of this sort.

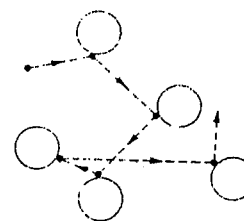


Fig. 1-8 Molecular free paths.

When molecules are passing through the thin layer of material in Fig. 1-6, the number removed from the beam by collisions is small compared with the original number, and we can say that N molecules have each traversed a thickness dx of material and that in the process a number dN of collisions have taken place. The total distance traveled by all of the N molecules is then $N dx$. We now make the hypothesis that the number of collisions made by a single molecule

in traversing the same total distance $N dx$ is equal to the number of collisions made by N molecules, each traversing a distance dx . Then from Eq. (1-35), the total number of collisions made by the single molecule in a total path length $N dx$ is

$$dN = Nn\sigma dx. \quad (1-38)$$

The mean free path of the molecule is equal to the total path length divided by the number of collisions, or

$$L = \frac{\text{total path length}}{\text{total number of collisions}}.$$

From the expressions above for the total path length and the total number of collisions, we have

$$L = \frac{N dx}{Nn\sigma dx} = \frac{1}{n\sigma}. \quad (1-39)$$

The concept of mean free path may be visualized by thinking of a man shooting a rifle aimlessly into a forest. Most of the bullets will hit trees, but some bullets will travel much farther than others. It is easy to see that the average distance the bullets go will depend inversely on both the denseness of the woods and the size of the trees.

In the above analysis, we assumed that the target molecules were at rest. This assumption is valid for a bullet molecule going through a solid. If, however, we consider a gas in which both the target and the bullet molecules are moving randomly, the mean free path will decrease because now there are not only head-on collisions as before, but also "sideswipes" with targets moving across the line of travel of the bullet. It is found that the mean free path of a molecule of an ideal gas having a Maxwellian distribution of speeds is

$$L = \frac{0.707}{n\sigma}. \quad (1-40)$$

1-11 FARADAY'S LAW OF ELECTROLYSIS—SKEPTICISM

Another line of argument supporting the atomic view of matter came from the work of Faraday. In 1833 he observed that if the same electric charge is made to traverse different electrolytes, the masses of the materials deposited on the electrodes are proportional to the chemical equivalent mass of the materials. The quantity of electricity required to deposit a mole of univalent ions in electrolysis is called the Faraday constant, F , and is equal to 9.64867×10^4 coulombs. Like the law of multiple proportions proposed by Dalton, this also implied atomicity of matter. Faraday's law, however, brings electricity into the picture and implies that both electricity and matter are atomic.

We have traced a few highlights of the development of the atomic view of matter through most of the nineteenth century, but since no one had ever seen

a molecule, the entire theory was still regarded with skepticism. Maxwell, who proposed the distribution of speeds already discussed, did his greatest work in electrical theory. It was he who found the relationship between electricity and light, and it is because of his work that we often call light "electromagnetic radiation." In his comprehensive book on electricity and magnetism (1873), after explaining Faraday's laws of electrolysis on the basis of the atomic theory of matter and electricity, Maxwell says, "It is extremely improbable that when we come to understand the true nature of electrolysis we shall retain in any form the theory of molecular charges, for then we shall have obtained a secure basis on which to form a true theory of electric currents and so become independent of these provisional theories."

As late as 1908 the physical chemist Wilhelm Ostwald and the physicist Ernst Mach opposed the atomic theory of matter. Their skepticism is an interesting question in epistemology. These scientists were unwilling to accept purely indirect evidence. Mach makes their position clear in the following analogy: A long elastic rod held in a vise may be made to execute slow, perceivable vibrations. If the rod is shortened, the vibrations become a blur in which individual motions of the rod cannot be followed. If the rod is shortened further, the blur may be visually unobservable but a tone is heard. If the rod is made so short that we no longer experience a physical sensation from its behavior, we may still think of it as vibrating when struck. This, according to Mach, is a safe extrapolation of our ideas because it proceeds from the *directly* observable to the *indirectly* observable. Those who were skeptical about the atomic theory objected to the fact that the evidence was *entirely indirect*. The experiments described in the next section provided the observable events which made the indirect evidence we have given acceptable to everyone.

1-12 PERRIN'S VERIFICATION OF THE ATOMIC VIEW OF MATTER : N_{AVO}

Credit for removing the remaining skepticism of atomic theory goes to the French physical chemist Perrin. He tested the hypothesis that the suspended particles which dance about in a stationary liquid in Brownian movement behave like large gas molecules. For his experiments, Perrin prepared a water suspension of particles which met a stringent set of requirements. They had to be large enough to be seen individually, but small enough to have an appreciable thermal motion which could be measured; and they had to be of known uniform size and mass. Further, the concentration of the particles in the suspension had to be so low that the force effects between them could be neglected. In short, the particles had to be directly observable and conform to the assumptions of the kinetic theory of gases. Perrin was able to obtain a suspension of particles that met these requirements by centrifuging a water mixture of powdered gamboge, a gum resin more dense than water. The centrifuge separated the particles according to size. After drawing off a portion of the mixture where

the magnitude of the particle size was suitable for his experiments, he could centrifuge again and again until the size of the remaining particles was nearly uniform. Although gamboge is more dense than water, Perrin observed that the particles did not settle out of still water. They assumed a distribution in height, with more particles per unit volume near the bottom of the container than at the top. He measured this distribution as a function of height.

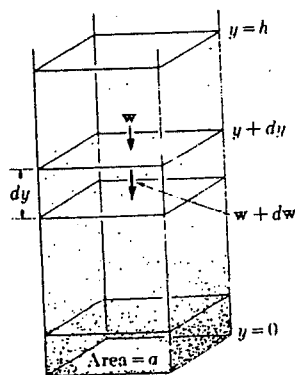


Fig. 1-9 Density distribution in a long column of gas in a gravitational field.

To derive the distribution equation, consider for the moment, instead of a water suspension, a vertical column of gas (Fig. 1-9) with cross-sectional area a and at a uniform temperature. Through this column, let us take a horizontal slice of thickness dy . If the weight of the gas above this slice is w , then the weight of the gas above the bottom of the slice will be $w + dw = w + mgn dy$, where mg is the weight of a molecule, n is the average number of molecules per unit volume, and $a dy$ is the volume of the slice. (Note that we are employing an atomic view of the gas.) The difference of these weights per unit area, $mgn dy$ is the pressure difference due to the gas in the slice, that is, $dp = -mgn dy$. The minus sign denotes that the pressure decreases as the height increases. Since the molecules in the column of gas have weight, the number of molecules per unit volume at a low level is greater than at a higher one. Because of this difference in concentration, there is a corresponding difference in the number of molecular collisions per unit time at the two levels, and the column of gas comes to dynamic equilibrium. In this state, the weight of the molecules in any layer is just balanced by the net upward force caused by the difference between the number of molecular impacts per unit time on the lower and upper horizontal surfaces of the layer. We shall next obtain an expression for the difference in pressure between two levels produced by a difference in molecular concentrations.

The equation $pV = RT$ holds for one mole of any gas that can be regarded

as ideal. According to atomic theory, the number of molecules in a mole is the Avogadro constant N_A . We can obtain an expression that contains the concentration of the molecules by dividing the ideal-gas law equation by the Avogadro constant. Thus we have

$$pV/N_A = RT/N_A \quad \text{or} \quad p = nkT,$$

where $n = N_A/V$ is the molecular concentration. This concentration is a function of the pressure and therefore, since k and T are constant, $dp = kT dn$. When this expression for the difference of pressure due to the difference in molecular concentrations in the layer of height dy is equated to the difference caused by the weight of the layer, we obtain

$$kT dn = -mgn dy \quad \text{or} \quad \frac{dn}{n} = -\frac{mg}{kT} dy. \quad (1-41)$$

Here m is the mass of a single molecule.

The relation between the molecular concentration n_0 at $y = 0$ and n at $y = h$ can be found by integrating Eq. (1-41). We have

$$\int_{n_0}^n \frac{dn}{n} = \int_0^h -\frac{mg}{kT} dy,$$

which gives

$$n = n_0 e^{-mgh/kT}. \quad (1-42)$$

Since the pressure of a gas is directly proportional to the number of molecules per unit volume, Eq. (1-42) can be rewritten in terms of pressures. The resulting equation is then called the *law of atmospheres*, since it gives the distribution in height of the pressure in a column of gas at constant temperature and subject to the force of gravity.

Equation (1-42) must be modified slightly to make it applicable to water suspensions. The effective weight of a particle suspended in a fluid is the resultant of its weight and Archimedes' buoyant force. The volume of a particle of mass m and density ρ is m/ρ and the mass of an equal volume of liquid having a density ρ' is $\rho'm/\rho$. Therefore, the buoyant force on this particle when submerged in the liquid is $m g \rho'/\rho$, and its effective weight becomes

$$mg - m g \frac{\rho'}{\rho} = mg \left(\frac{\rho - \rho'}{\rho} \right).$$

When we replace the actual weight mg in Eq. (1-42) by the effective weight and reinsert instead of the Boltzmann constant $R/N_A = k$, we obtain

$$n = n_0 \exp \left[-\frac{N_A m g (\rho - \rho') h}{\rho R T} \right]. \quad (1-43)$$

This is the equation for *sedimentation equilibrium* of a suspension as a result of Brownian movement.

Perrin measured a series of n 's at a series of h 's in a very dilute suspension. The results verified the sedimentation equation. Equally important, his measurements yielded a value for N_A , since all other quantities in the equation were known. The very existence of the Avogadro constant implies the correctness of the atomic theory.

It is interesting that Einstein, the greatest contributor to the development of modern physics, also had a part in the final establishment of the atomic theory. In 1905 he derived an equation which describes how a suspended particle should migrate in a random manner through a liquid. His expression involved the Avogadro constant, and Perrin's verification of the Einstein formula confirmed the value of this constant. The results showed that small particles suspended in a stationary liquid do move about in the manner predicted by the molecular-kinetic theory of gases.

Altogether, Perrin used four completely independent types of measurements, each of which was an observable verification of atomic theory and each of which gave a quantitative estimate of the Avogadro constant. Since the publication of his results in 1908, no one has seriously doubted the atomic theory of matter.

1-13 BOLTZMANN'S DISTRIBUTION LAW

Maxwell's speed-distribution law (Eq. 1-21) and the law of atmospheres (Eq. 1-42) have something in common. In both formulas the factor $\exp(-E/kT)$ appears, where E in one case is the kinetic energy $\frac{1}{2}mv^2$ of a molecule and in the other is the potential energy mgh of a molecule in a gravitational field. The similarity is by no means accidental. Both formulas referred to can be derived from a general law of statistical mechanics called Boltzmann's distribution law:

$$n = n_0 e^{-(E - E_0)/kT} \quad (1-44)$$

The law deals with the distribution of molecules or other particles over different energy states with $E - E_0$ being the difference in energies between these states. The *a priori* distribution over the states, i.e., the distribution that would exist without any energy difference, must be uniform.

Let us consider the example of the law of atmospheres. Assume that the molecules in Fig. 1-9 are in an enclosed box with walls at temperature T . In the absence of a gravitational field, the distribution of molecules would be uniform (on the average). This means that there would be the same number in the state identified by a position between $y = 0$ and dy as in the state identified by a position in the equally large volume element between h and $h + dy$. If we now "turn on" the gravitational field and maintain the temperature T on all walls, the difference in potential energy between the two states defined above will be $E - E_0 = mgh$. Inserting this into Eq. (1-44), we obtain Eq. (1-42). Strictly speaking, the kinetic energy should also have been included in the

description of the energy states. In the particular example discussed, the kinetic energy distribution is the same in the two volume elements. (The temperature is the same.) Therefore we need not consider the kinetic energy.

Maxwell's speed-distribution law can be derived from Eq. (1-44) by postulating that the *a priori* distribution of molecules in velocity space is uniform. This means that the density of dots in Fig. 1-3(a) would be uniform, without the influence of the kinetic-energy difference on the exponential of Eq. (1-44).

Boltzmann's distribution law can be derived by maximizing the entropy of a system of particles with a constant total energy.* It is beyond the scope of this book to include this derivation.

PROBLEMS

- 1-1 An early chemist wishes to determine the atomic weight of nitrogen. He assumes that the atomic weight of oxygen is exactly 16, and he prepares four oxides of nitrogen which are distinctly different compounds (see data below).

Nitrogen, parts by weight	Oxygen, parts by weight	Product oxide
86.3	197	A
500	285	B
300	343	C
108.2	186	D

- a) Show that these data demonstrate the law of multiple proportions. (Hint: First find the masses of one of these elements that unite with a unit mass of the other.) b) The chemical formulas of the products cannot be determined completely from the above data, but, by assuming that nature is simple, one may propose several possible sets of product formulas. Write out several possible sets of product formulas. c) Calculate the atomic weight of nitrogen for each set.
- 1-2 Compute the molar heat capacity at constant volume of a gas composed of molecules that are rigid three-dimensional structures.
- 1-3 Given that p represents the density of a gas, show that

$$v_{rms} = \sqrt{3p/\rho}.$$

- 1-4 a) Compute the arithmetic mean speed and the root-mean-square speed for each of the following distributions of the speeds of eight particles:
1. All eight have speeds of 10 ms^{-1} .
 2. Two have speeds of 3 ms^{-1} , four have speeds of 6 ms^{-1} , and two have speeds of 10 ms^{-1} .

* See, for instance, D. L. Livesey, *Atomic and Nuclear Physics*. Waltham, Mass.: Blaisdell, 1966, p. 13.

3. One has a speed of 3 ms^{-1} , three have speeds of 6 ms^{-1} , and four have speeds of 10 ms^{-1} .

4. Four are at rest and four have speeds of 10 ms^{-1} .

b) In each case decide whether the shape of the graph of the speed distribution would be the same as that of the translational kinetic-energy distribution, assuming that each particle has the same mass.

1-5 The speed distribution function of a group of N particles is given by $dN_v = av dv$, where dN_v is the number of particles that have speeds between v and $v + dv$, and a is a constant. No particle has a speed greater than V , and the speeds range from 0 to V . a) Draw a graph of the distribution function, that is, plot (dN_v/dv) versus v . b) Find the constant a in terms of N and V . c) Compute the average speed, the root-mean-square speed, and the most probable speed in terms of V . d) What percent of the particles have speeds between the average speed and V ? between the root-mean-square speed and V ?

1-6 a) Show from Eq. (1-31) that the most probable speed in a Maxwellian distribution is given by

$$v_m = \sqrt{2kT/m} = \sqrt{2RT/M},$$

and b) then show from Eq. (1-18) that $v_m = \sqrt{2/3} v_{\text{rms}}$. (Hint: Determine the condition for which the ordinate quantity in Fig. 1-2 is maximum.)

1-7 Show from Eq. (1-31) that the average speed in a Maxwellian distribution is

$$\bar{v} = \int_0^\infty (\Delta N_v) v dv / \int_0^\infty (\Delta N_v) dv = \sqrt{8kT/m}.$$

Some definite integrals are

$$\int_0^\infty x^2 e^{-ax^2} dx = (\sqrt{\pi}/4)a^{-3/2},$$

$$\int_0^\infty x^3 e^{-ax^2} dx = 1/2a^2,$$

$$\int_0^\infty x^4 e^{-ax^2} dx = (3\sqrt{\pi}/8)a^{-5/2}.$$

1-8 Show from Eq. (1-31) that the root-mean-square speed in a Maxwellian distribution is

$$v_{\text{rms}} = \left[\int_0^\infty (\Delta N_v) v^2 dv / \int_0^\infty (\Delta N_v) dv \right]^{1/2} = \sqrt{3kT/m}.$$

1-9 The speed of propagation of a sound wave in air at 27°C is about 348 ms^{-1} . Find the ratio of this speed to the rms speed of nitrogen molecules at this temperature.

1-10 The drum of a Zartman-Ko apparatus (Fig. 1-4), has a radius of 8 cm and rotates at 6000 rpm. The oven contains mercury atoms at a temperature of 600 K. Two atoms of mercury, one with the most probable speed at oven temperature and the other with the rms speed at the same temperature, leave the oven and enter the rotating drum. These two atoms are then deposited on the

glass plate at the far side of the drum. What is the separation of these two atoms on the glass plate? (Atomic weight of mercury = 200.6.)

1-11 An object can escape from the surface of the earth if its speed is greater than $\sqrt{2gR}$, where g is the acceleration caused by gravity and R is the radius of the earth. a) Using a radius of $6.4 \times 10^6 \text{ m}$, calculate this escape speed. b) Explain why oxygen and nitrogen remain in the earth's atmosphere while hydrogen does not.

1-12 a) At what temperature will the rms speed of oxygen molecules be twice their rms speed at 27°C ? b) At what temperature will the rms speed of nitrogen molecules equal the rms speed of oxygen molecules at 27°C ?

1-13 a) To what temperature would an ideal gas in which the "particles" are baseballs have to be heated so their rms speed in a Maxwellian distribution would equal that of a fast ball having a speed of 30.5 ms^{-1} ? (The mass of a baseball is 144 g.)

1-14 Find the rms speed, the average speed, and the most probable speed of the molecules of gaseous hydrogen at a temperature of (a) 20°C and (b) 120°C .

1-15 Assuming that the energy E of a molecule is only translational kinetic energy, a) show from Eq. (1-31) that the fractional number of molecules which have energies in the range ΔE is

$$\frac{\Delta N}{N} = \frac{2}{\sqrt{\pi}} \left(\frac{1}{kT} \right)^{3/2} E^{1/2} e^{-E/kT} \Delta E.$$

b) From the energy distribution of part a), show that the most probable energy is kT . c) What is the ratio of the average translational kinetic energy to the most probable translational kinetic energy?

1-16 Show that the kinetic energy of translation of a molecule having the most probable speed in a Maxwellian distribution is equal to kT .

1-17 A neutron is a fundamental particle. Like ordinary gas molecules, neutrons have a distribution of speeds, and this distribution is of prime importance in the theory of nuclear reactors. Quantitatively, a thermal neutron is usually defined as one having the most probable speed of a Maxwellian distribution at 20°C . Find a) the kinetic energy of translation and b) the speed of a thermal neutron. c) A thermal neutron is sometimes called a " kT neutron." Why? (The mass of a neutron is 1.0087 u.)

1-18 Assume that hydrogen atoms in the atmosphere of the sun obey the Maxwellian speed distribution. a) Given that the temperature is 6000°K , calculate the kinetic energy of one of these atoms moving with the most probable speed in the distribution. b) Calculate the speed of this atom.

1-19 When the atoms in a deuterium gas have an average translational kinetic energy of $12 \times 10^{-14} \text{ J}$, they can approach one another so closely that nuclear fusion will occur. a) What is the speed of a deuterium atom having this kinetic energy? b) To what temperature would the deuterium gas have to be heated so that the rms speed of the atoms would equal the speed in the preceding part? (Deuterium is hydrogen having an atomic weight of 2.014.)

ENGE 2+3

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INTRODUCTION TO ATOMIC PHYSICS

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SEZIONE STAT. AGGREGATI
E BIOMOLECOLE



ADDISON-WESLEY PUBLISHING COMPANY
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- 1-20 a) What is the total kinetic energy of translation of the atoms in 4 moles of helium at a temperature of 27°C ? b) What would be the answer for the same amount of another ideal gas?
- 1-21 The microscopic cross section for a certain bullet and particle is σ when they are electrically neutral. Would the effective value of σ increase or decrease if the bullet and particle carried electric charges a) of like sign, b) of unlike sign?
- 1-22 a) Show that n , the number of molecules per unit volume of an ideal gas, is given by $n = pN_A/RT$, where N_A is the Avogadro constant. b) Find the number of molecules in 1 m^3 of an ideal gas under standard conditions. c) What is the number of molecules in 1 m^3 of an ideal gas at a pressure of two atmospheres and a temperature of 47°C ? (1 atmosphere = $1.013 \times 10^5\text{ N m}^{-2}$).
- 1-23 a) If the pressure is kept constant, at what temperature will the mean free path of the molecules of a given mass of an ideal gas be twice that at 27°C ? b) If the temperature is kept constant, at what pressure in millimeters of mercury will the mean free path of the molecules of a given mass of an ideal gas be 1000 times greater than that at a pressure of 1 atm?
- 1-24 The molecular diameter of all diatomic gases is approximately $2 \times 10^{-10}\text{ m}$. a) Find the mean free path for a Maxwellian distribution of speeds of the molecules of hydrogen gas when at a pressure of 1 atm and a temperature of 20°C . (Data for calculating the macroscopic cross section are given in Problem 1-22.) b) How many collisions per second would a molecule that is always moving with the average speed in a Maxwellian distribution make in the preceding case? (The time of contact during collisions is negligible.) c) What is the ratio of the mean free path in part a) to the wavelength of green light, $\lambda = 5500 \times 10^{-10}\text{ m}$?
- 1-25 A beam of bullet particles is incident normally on a layer of material containing stationary target particles. Find a) the fraction of the incident beam transmitted and the fraction which experienced collisions in a layer whose thickness equals the mean free path and b) the thickness of the layer in terms of the mean free path required to reduce the transmitted beam to one-half the intensity of the incident beam.
- 1-26 In one of his experiments, using a water suspension of gamboge at 20°C , Perrin observed an average of 49 particles per unit area in a very shallow layer at one level and 14 particles per unit area at a level $60\text{ }\mu$ higher. The density of the gamboge was 1.194 g cm^{-3} and each particle was a spherical grain having a radius of $0.212\text{ }\mu$. ($1\text{ }\mu = 10^{-6}\text{ m}$.) Find a) the mass of each particle, b) the Avogadro constant, and c) the molecular weight of a particle if each grain is regarded as a single giant molecule. Use the results from parts a) and b) to calculate c).

The Atomic View of Electricity

2-1 ELECTRICAL DISCHARGES

We have already considered how Faraday's law of electrolysis implies that both matter and electricity are atomic. In spite of Maxwell's skepticism, it is very difficult to explain the fact that the passage of one faraday of electricity through an electrolyte liberates or deposits an equivalent weight of a substance, except by assuming that both matter and electricity exist in units which preserve their identity throughout the process.

In order to learn more about "particles of electricity," we turn to another line of investigation and consider the passage of electricity through gases. Although Benjamin Franklin's very dangerous experiment with kite and key was not a particularly convincing one, it nevertheless led to the correct conclusion that lightning is the discharge of electricity through a gas (air). Every electric spark is an example of this process. Since sparks are one of the most dramatic electric effects, it is natural that they should have been a subject of early study.

The passage of electricity through gases is a very complicated process and a great deal has been learned from it. There are many ways in which the character of an electrical discharge can be altered, but here we shall direct our attention to the effect of gas pressure. A typical discharge tube is shown in Fig. 2-1. This system has a gauge which measures the gas pressure and a pumping system which varies the pressure. Electrodes are sealed into the ends of the tube so that an electric field can be established between them.

When the pressure in the tube is atmospheric, a very large electric field is required to produce a discharge (about $3 \times 10^6\text{ V m}^{-1}$ for air). The discharge is a violent spark as the gas suddenly changes from being an excellent insulator to being a good conductor. As the pressure is reduced, the discharges are more easily established (Fig. 2-2), until, at very low pressures, they again become

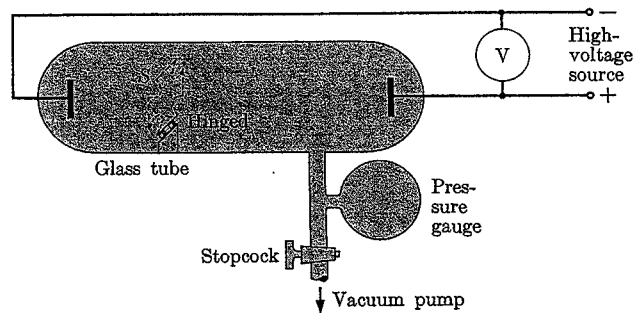


Fig. 2-1 Gas discharge apparatus.

difficult to start. Discharges start most easily at a pressure of about 2 mm of mercury (although this will depend upon the kind of gas and the geometry of the electrodes). As the pressure is reduced, the discharge changes in character. With air in the tube, the bright spark changes to a purple glow filling the whole tube, and with neon, one obtains the red glow seen in many advertising signs. On further lowering of the pressure, the glow assumes a remarkable and complicated structure, with striations and dark spaces. At very low pressures the glow of the gas becomes dim and a new effect appears—the glass itself begins to glow. If the bulb has within it a device which is hinged so that it can be made

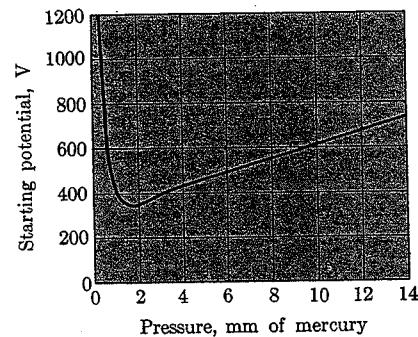


Fig. 2-2 Typical starting potential curve of gaseous discharge.

to move into or out of the region between the electrodes by tipping the entire bulb (*S* in Fig. 2-1), then another effect may be seen. The greenish glow of the glass, which appears everywhere between the electrodes when the object *S* is out of the way, is partly obliterated when *S* is swung between the electrodes. If the object *S* has some distinctive shape, it may be seen clearly that it is casting a shadow. The shadow is on the side of *S* that is away from the negative elec-

trode or cathode. If the cathode is small, the shadow is rather sharp. It is a simple deduction that the greenish glow is caused by some kind of rays from the cathode that cannot penetrate the obstruction *S*. These rays are called *cathode rays*. Many years ago it was observed that these rays could be deflected by both electric and magnetic fields, and the direction of these deflections showed that the rays were negatively charged.

Sir J. J. Thomson undertook a quantitative study of cathode rays in 1897. He was able to show that all cathode rays or corpuscles possess a common property. He showed that the ratio of their charge to their mass, q/m , was a constant. His measurements did not establish that all the rays have identical charges or identical masses, although this is the simplest interpretation of his results. He did, however, discover a unique characteristic of these rays and he is regarded as the discoverer of a fundamental particle of electricity, the electron.

2-2 NONRELATIVISTIC CHARGED-PARTICLE BALLISTICS

Before discussing one of the methods by which q/m can be measured, let us review some basic facts about the motion of charged particles in electromagnetic fields. When a particle having charge $+q$ is in an electric field of intensity E , the particle experiences a force in the direction of the field, of magnitude

$$F = qE. \quad \text{OK} \quad (2-1)^*$$

If all other forces on the particle are negligible compared with this one, the particle will undergo accelerated motion, and we have by Newton's second law

$$\frac{dp}{dt} = qE, \quad \text{OK} \quad (2-2)$$

where p is the momentum of the particle. Unless the velocity of the particle is very high, we can in practice use nonrelativistic mechanics and write $dp/dt = ma$, yielding

$$ma = qE. \quad \text{OK} \quad (2-3)$$

When a particle of charge q moves in a magnetic field of induction B with a velocity v , it experiences a force that is perpendicular to the plane formed by the vectors B and v :

$$F = qv \times B. \quad \text{OK} \quad (2-4)$$

* This equation and those following are valid in any consistent system of units. No conversion factors for units need be introduced provided *all* are electrostatic units, *all* are electromagnetic units, or *all* are meter-kilogram-second-ampere units. This will be true of all equations in this book except in cases where units peculiar to atomic physics, such as angstrom units or electron volts, are specified.

If the velocity vector is parallel to the magnetic field, clearly no force results and therefore there is no change in the motion. When the velocity vector points in any other direction, we can break it up into two components, one parallel to the field v_{\parallel} , and one perpendicular to the field v_{\perp} . The component v_{\perp} gives rise to a force $F = qv_{\perp}B$, perpendicular to v_{\perp} , and this force therefore produces a circular motion. If the component v_{\parallel} is nonzero, the result is a helix rather than a circular orbit. Both components and the total speed are numerically constant, but v_{\perp} continuously changes direction. By use of Newton's second law, we find

$$qv_{\perp}B = mv_{\perp}^2/R, \quad qBR = mv_{\perp}. \quad (2-5)$$

We have here used the formula for the centripetal acceleration $a_c = v^2/R$. Equation (2-5) is valid also in relativistic mechanics (Appendix 3), when m is taken as the relativistic mass. This is true because the speed does not change and therefore the mass is constant.

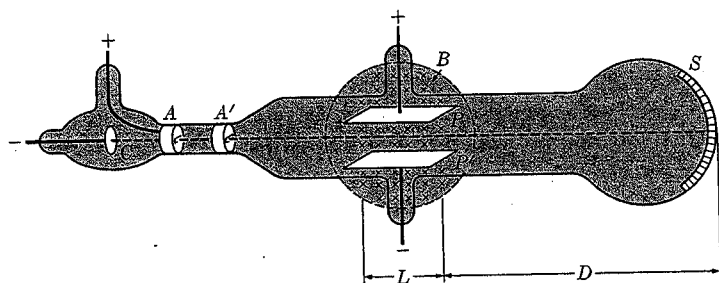


Fig. 2-3 Thomson's apparatus for measuring the ratio q/m for cathode rays.

2-3 THOMSON'S MEASUREMENT OF q/m

We are now ready to consider how Thomson measured the ratio of charge to mass, q/m , for what he called "cathode corpuscles." His apparatus (Fig. 2-3) consisted of a highly evacuated glass tube into which several metal electrodes were sealed. Electrode C is the cathode from which the rays emerged. Electrode A is the anode, which was maintained at a high positive potential so that a discharge of cathode rays passed to it. Most of the rays hit A, but there was a small hole in A through which some of the rays passed. These rays were further restricted by an electrode A' in which there was another hole. Thus a narrow beam of the rays passed into the region of the two plates P and P'. After passing between the plates, the rays struck the end of the tube, where they caused fluorescent material at S to glow.

The deflection plates P and P' were separated a known amount, so that when they were at a known difference of potential the electric field between

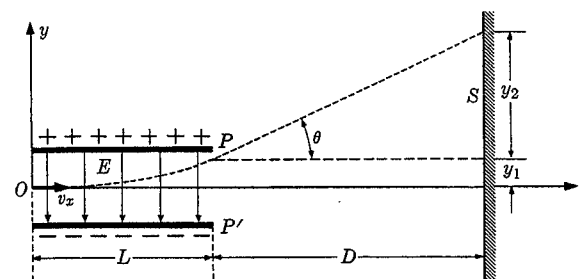


Fig. 2-4 Electrostatic deflection of cathode rays.

them could be computed. We shall assume that the field was uniform for a distance L between the plates and zero outside them. When the upper plate P was made positive, the electric field deflected the negative cathode rays upward.

In Fig. 2-4, the cathode rays are assumed to enter the region between the plates at the origin O with a velocity v_x . Because there is no force component in the x-direction, v_x remains constant.* The general equation for displacement in uniformly accelerated motion is

$$s = s_0 + v_0 t + \frac{1}{2} a t^2. \quad (\text{formula of Kinematics}) \quad (2-6)$$

Applying Eq. (2-6) to the horizontal direction, we obtain

$$x = v_x t. \quad (2-7)$$

Between the plates the rays experience an upward acceleration,

$$a_y = \frac{qE}{m}, \quad (2-8)$$

obtained from Eq. (2-3). The electric field E is constant, since the fringing-field zone is neglected, and it is equal to the potential difference between the deflection plates divided by their separation. Hence the general displacement equation in the vertical direction becomes

$$y = \frac{qEt^2}{2m}. \quad (y = \frac{1}{2} a t^2) \quad (2-9)$$

Elimination of t between Eqs. (2-7) and (2-9), yields the equation for the

* Strictly speaking, this is not true. When the particles leave the region of the plates with a y -displacement as shown, they will experience a decelerating force in the x -direction. (The field lines in the fringing field bulge out rather than being vertical as shown.) The effect is of the exact magnitude required to conserve the energy of the particles; that is, the speed after the deflector equals the speed before the deflector. If $v_y \ll v_x$, we can neglect this effect for the present discussion.

parabolic trajectory.

*ce se la sovrapposizione in funzione di altre
e sostituisce in $y = \dots$, ottenendo la
traiettoria*

$$y = \frac{qEx^2}{2mv_x^2} \quad (2-10)$$

The quantity y_1 , defined in Fig. 2-4, is the value of y when $x = L$.

Beyond the plates, the trajectory is a straight line because the charge is then moving in a field-free space. The value of y_2 is $D \tan \theta$, where D and θ are defined as in Fig. 2-4. The slope of this straight line is

$$\tan \theta = \left(\frac{dy}{dx} \right)_{x=L} = \left(\frac{qEx}{mv_x^2} \right)_{x=L} = \frac{qEL}{mv_x^2} \quad (2-11)$$

The total deflection of the beam, y_E , is $y_1 + y_2$, so that

$$y_E = y_1 + y_2 = \frac{qEL^2}{2mv_x^2} + \frac{qELD}{mv_x^2} = \frac{qEL}{mv_x^2} \left(\frac{L}{2} + D \right) \quad (2-12)$$

*serve un'altra
eq. con v_x , così
e eliminiamo q/m* If q/m is regarded as a single unknown, then there are two unknowns in this equation. The initial velocity of the rays, v_x , must be determined before q/m can be found. We need another equation involving the initial velocity v_x , so that this unknown velocity can be eliminated between the new equation and Eq. (2-12).

Thomson obtained another equation by applying a magnetic field perpendicular to both the cathode-corpuscule beam and the electric field. It is represented in Fig. 2-3 as being into the page and uniform everywhere within the x-marked area. Thus the electric and magnetic forces acted on the cathode rays in the same geometric space.

Figure 2-5 shows the situation when the magnetic field alone is present. The negatively charged rays experience a force that is initially downward. This force is not constant in direction, but is always normal to both the field and the direction of motion of the rays. Therefore the cathode corpuscles move in a circular path according to Eq. (2-5). The center of curvature of the trajectory is at C , and the radius of curvature of the path is

$$R = mv_x/qB, \quad (2-13)$$

where v_x is the initial velocity of the rays in the x-direction. Referred to the origin O , the equation of this circular path is

$$x^2 + (R + y)^2 = R^2. \quad (2-14)$$

Solving for R , we get

$$R = -\frac{x^2 + y^2}{2y} \approx -\frac{x^2}{2y} \quad (2-15)$$

The approximation is good if the deflection is small compared with the distance the rays have moved into the magnetic field, that is, when $y^2 \ll x^2$.

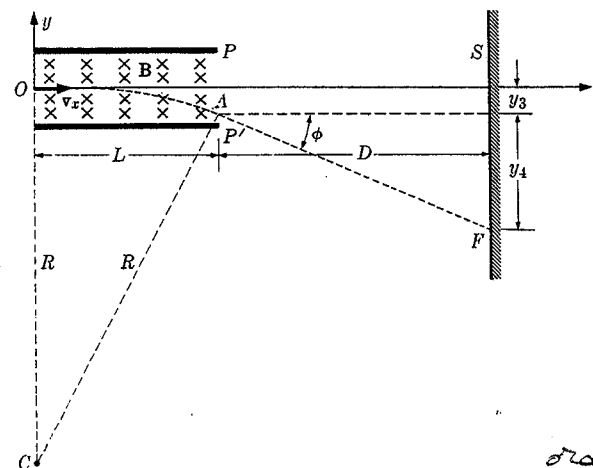


Fig. 2-5 Magnetic deflection of cathode particles.

*ora fare la stessa cosa
per il caso in cui c'è solo B*

Since the radius of curvature is difficult to measure, we eliminate R between Eqs. (2-13) and (2-15), and obtain

$$y = -\frac{qBx^2}{2mv_x} \quad (2-16)$$

Therefore, for small deflections, the circular path may be approximated by the parabolic path of Eq. (2-16). The minus sign indicates that the curve is concave downward.

Just as in the electric case, we find that y_3 is the value of y for $x = L$. The rays again move in a straight line through the field-free region, so that

$$y_4 = D \tan \phi = D \left(\frac{dy}{dx} \right)_{x=L} = -\frac{DqBL}{mv_x} \quad (2-17)$$

For the total magnetic deflection y_B , we have

$$y_B = y_3 + y_4,$$

or

$$y_B = -\frac{q}{m} \left(\frac{BL^2}{2v_x} + \frac{BLD}{v_x} \right) = -\frac{qBL}{mv_x} \left(\frac{L}{2} + D \right) \quad (2-18)$$

Equation (2-18) is very similar to Eq. (2-12). It contains q/m and v_x together with measurable quantities, so that v_x can be eliminated and q/m found. It is interesting, however, to follow Thomson's procedure for determining v_x by considering the simultaneous application of the electric and the magnetic fields. If these are adjusted so that there is no deflection on the screen, then the force of the electric field on the charged particle is balanced

YES

oppose use $E \neq B$ in order to create equilibrium by that of the magnetic field. For this condition of balance, we find from Eqs. (2-1) and (2-3) that

$$F = qE - qv_x B = 0, \quad (2-19)$$

or, in terms of v_x ,

$$v_x = E/B. \quad (2-20)$$

For this particular ratio of the fields, the particle goes straight through both fields. It is undeflected, and therefore the measurement of v_x does not depend on the geometry of the tube. Since $y = 0$ at all times, the approximation in Eq. (2-15) is avoided. The velocity thus determined may be substituted into Eq. (2-12), which was derived without approximation.

Thomson measured q/m for cathode rays and found a unique value for this quantity which was independent of the cathode material and the residual gas in the tube. This independence indicated that cathode corpuscles are a common constituent of all matter. The modern accepted value of q/m is $(1.758803 \pm 0.000005) \times 10^{11}$ coulombs per kilogram. Thus Thomson is credited for the discovery of the first subatomic particle, the electron. Because it was shown later that electrons have a unique charge e , the quantity he measured is now denoted by e/m_e . He also found that the velocity of the electrons in the beam was about one-tenth the velocity of light, much larger than any previously measured material particle velocity.*

The electrons Thomson studied had nearly equal velocities. If this had not been the case, the spot on the end of his experimental tube would have been seriously smeared. The reason why the velocities were nearly equal is, of course, that they had been accelerated through the same potential difference, starting from practically zero velocity. Let V be the potential difference between the cathode and the anode, and let the average potential of P and P' and the potential of A' and S be the same as that of A (Fig. 2-3). We then get by conservation of energy:

$$qV = \frac{m}{2} v_x^2,$$

or

$$q/m = e/m_e = v_x^2/2V. \quad (2-21)$$

This is another equation relating e/m_e and v_x . It could have been used with Eq. (2-18) to give e/m_e . Thomson could have measured the potential difference between the cathode and anode and been spared either the electric or magnetic deflection of the beam in the vicinity of P and P' . Indeed, other methods of measuring e/m_e utilize this principle.

* As shown in Appendix 3, relativistic effects are important when v^2/c^2 is not negligibly small, with c being the velocity of light. The errors introduced here (in Eq. 2-12) by using classical mechanics are of the order of magnitude of v^2/c^2 , or about 1 percent.

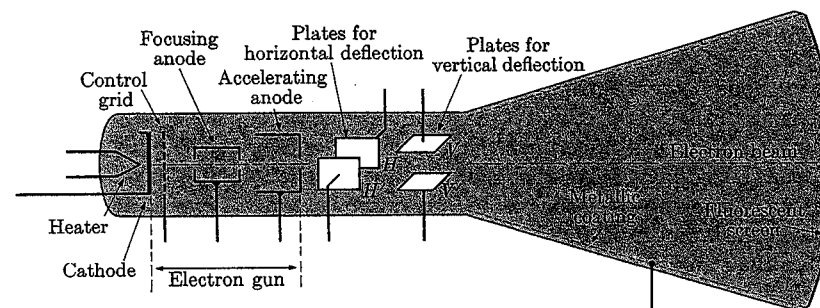


Fig. 2-6 Basic elements of a cathode-ray tube.

Cathode-ray tubes such as Thomson used have been developed into important modern electronic components. Electrostatic deflection of an electron beam is used in the cathode-ray tube of modern oscilloscopes. Such tubes usually have two sets of deflecting plates (Fig. 2-6), so that the electron beam can be deflected right and left as well as up and down. These tubes utilize the fact that the deflection is proportional to the electric field between the plates, as shown by Eq. (2-12). Television tubes, on the other hand, commonly utilize magnetic deflection to cause the beam to sweep over the face of the picture area.

Anyone can demonstrate for himself that electric and magnetic fields deflect electron beams. Holding a strong permanent magnet near the face of a television picture produces weird distortions. Rubbing the face of a picture tube or even the plastic protective window with wool, silk, or nylon will produce strong electric fields when the humidity is low. Neither the magnetic nor electric fields thus produced are uniform or perpendicular to the beam, and the deflections they produce are striking in their unpredictability.

2-4 ELECTRONIC CHARGE

Although the measurement of e/m_e indicated the identity of electrons, another measurement was required before e and m_e could be known separately. This was first made with precision in 1909 by R. A. Millikan, who perfected a technique suggested by J. J. Thomson and H. A. Wilson.

Both the charge e and the mass m_e of an electron are incredibly small quantities. The mass of any body can be determined from the measurement of the force acting on it when it is accelerated. Even if a single electron could be isolated for study, no instrument could measure its mass directly. Similarly, the charge on a body can be determined by measuring the force it experiences in an electric field. This method does not require the isolation of a single electron and, since very intense electric fields can be created, a measurable force can be produced.

An experiment to measure e must be carried out with a body having so few charges that the change of one charge makes a noticeable difference. Since the

experiment must be done with very little charge, the force the body experiences will be small even though a large electric field is utilized. If the force on the charged body is very small, then the body itself must be very light. The force of gravity is always with us, and if the small electric force is not to be masked by a large gravitational force, then the mass of the body must be both small and known. If the body is small enough that the electric force on its charges is of the same order of magnitude as the gravitational force it experiences, then it may be that the gravitational force will be a useful standard of comparison rather than an annoying handicap.

Millikan used a drop of oil as his test body. It was selected from a mist produced by an ordinary atomizer. The drop was so small that it could not be measured optically, but with a microscope it could be seen as a bright spot because it scattered light from an intense beam, like a minute dust particle in bright sunlight.

When such a drop falls under the influence of gravity, it is hindered by the air it passes through. The way in which the fall of a small spherical body is hindered by air had been described by Stokes, who found that at low velocities such a body experienced a resisting force R proportional to its velocity, or

$$R = kv. \quad (2-22)$$

The proportionality constant k was found by Stokes to be

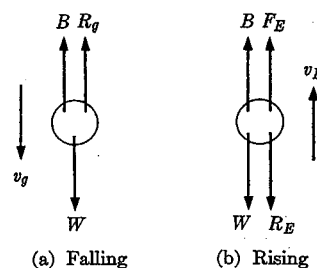
$$k = 6\pi\eta r, \quad F = 6\pi\eta r v \quad (2-23)$$

where η is the coefficient of viscosity of the resisting medium and r is the radius of the body. (This law assumes that the resisting medium is homogeneous. A more complicated law must be used if the size of the body is of the same order of magnitude as the mean free path of the molecules of the medium.) This is a friction equation very different from that introduced in mechanics to describe the force between two sliding bodies. In that case we assumed that the friction force depended only on the nature of the sliding surfaces and the normal force pressing the surfaces together. Hence in mechanics we discussed a force which did not depend on the speed of the motion. In the problem of a box sliding against friction down an inclined plane, the friction produced a constant force opposing the motion, but the acceleration was constant and the velocity increased continuously. A body subject to a frictional force like that given by Stokes' law will behave very differently.

A falling droplet of oil is acted on by its weight w , the buoyant force B of the air, and the resisting force $R = kv$ (Fig. 2-7). The resultant downward force F is

$$F = w - B - kv. \quad (2-24)$$

Initially, the velocity v is zero, the resisting force is zero, and the resultant downward force equals $w - B$. The drop therefore has an initial downward



(a) Falling

(b) Rising

Fig. 2-7 Forces acting on an oil drop (equilibrium conditions).

acceleration. As its downward velocity increases, the resisting force increases and eventually reaches a value such that the resultant force is zero. The drop then falls with a constant velocity called its terminal velocity, v_g . Since $F = 0$ when $v = v_g$, we have from Eq. (2-24),

$$w - B = kv_g. \quad (2-25)$$

Let ρ be the density of the oil and ρ_a the density of the air. Then

$$w = \frac{4}{3}\pi r^3 \rho g, \quad B = \frac{4}{3}\pi r^3 \rho_a g, \quad (2-26)$$

and inserting the value of k from Eq. (2-23), we get

$$\frac{4}{3}\pi r^3 (\rho - \rho_a) g = 6\pi\eta r v_g. \quad (2-27)$$

All of the quantities in this equation except r are known or measurable. We can therefore solve for the drop radius r and hence can express the proportionality constant k in terms of known or measurable quantities. The result is

$$k = 18\pi \left[\frac{\eta^3 v_g}{2g(\rho - \rho_a)} \right]^{1/2}. \quad (2-28)$$

With this constant known, we can use velocity measurement to determine forces. In the experiment, the oil drop is situated between two horizontal plates where a known strong electric field may be directed upward or downward or may be turned off (Fig. 2-8). The droplet has a small electric charge q

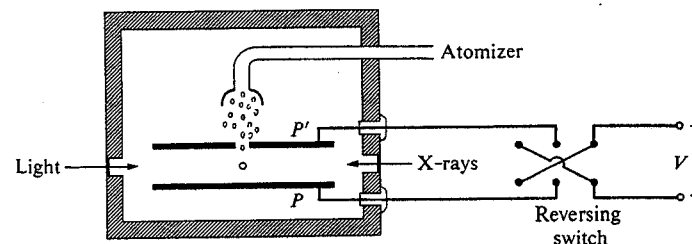


Fig. 2-8 Millikan's oil-drop experiment.

all initial accelera \in no F_{Stokes} $\because v=0$
 poi la resistenza aumenta, fino a
 che $F_{\text{Tot}} = 0 \Rightarrow v_{\text{finale}}$

which may be minus or plus, depending on whether it has an excess or deficiency of electrons. The droplet gets this charge from rubbing against the nozzle of the atomizer and from encounters with stray charges left in the air by cosmic rays, deliberately produced by x-rays, or by bringing a radioactive material nearby. In the electric field the drop will experience a force qE , which can always be directed upward by the proper choice of the direction of E . The experimenter can turn E on and off so that the drop falls by gravity or rises because of a dominating electric force in the region between the plates but never touches either.

The microscope with which the drop's movements are followed is equipped with two horizontal hairlines whose separation represents a known distance along the vertical line in which the drop travels. By timing the trips of the drop over this known distance, the terminal velocities of the drop are found. The velocities of fall, v_g (positive down), are all the same, since oil does not evaporate noticeably, and therefore the weight of the drop is constant. The velocity of rise, v_E (positive up), however, depends on the charge q and upon E . The resultant force on the drop while it is rising (Fig. 2-7(b)) is

$$F = qE + B - w - kv. \quad (2-29)$$

When the terminal velocity v_E is reached, the resultant force is zero, so

$$qE = w - B + kv_E. \quad (2-30)$$

But from Eq. (2-25), $w - B = kv_g$, so finally

$$q = \frac{k}{E} (v_g + v_E). \quad (2-31)$$

Since these terminal velocities are constant, they are relatively easy to measure.

Equation (2-31) permits the evaluation of q , the charge on the drop. In the oil-drop experiment, the value of v_g is determined for a particular drop with the electric field off, and a whole series of v_E 's for the same drop is observed with the field on. If we knew that the electronic charge was unique and that there was only one charge on the drop, then Eq. (2-31) would give the value of this charge at once. Since the nature of the electronic charge was not known, Millikan repeated the experiment with many different charges on the drop. This provided a set of q 's which he found to be integral multiples of one charge which he took to be the ultimate unit of charge, e . Thus he established the law of multiple proportions for electric charges and concluded from it that electricity must be atomic in character.

Millikan made observations on oil drops of different sizes and also on drops of mercury. In one instance a drop was watched continuously for eighteen hours. The sets of observations always gave the same value of the electronic charge or "atom" of electricity. The best modern determination of e is $(1.602192 \pm 0.000007) \times 10^{-19}$ C.

2-5 MASS OF THE ELECTRON; AVOGADRO CONSTANT

Since e/m_e and e are now known, it is only simple arithmetic to find the mass of the electron to be

$$m_e = (9.10956 \pm 0.00005) \times 10^{-31} \text{ kg.}$$

Still another basic atomic constant may now be calculated with precision by using the value of the electronic charge. The Faraday constant is the amount of charge required to transport one atomic (molecular) mass of a univalent ion of a material through an electrolyte. Dividing the Faraday constant by e gives the number of electrons which have participated in this transport, or the Avogadro constant. The result agrees with Perrin's value, which had finally established the atomic view of matter.

2-6 POSITIVE RAYS

After the particle of negative electricity, the electron, had been identified, it was reasonable to ask about positive electricity. The search was made in a discharge tube very similar to that which disclosed cathode rays. In 1886, Goldstein observed that if the cathode of a discharge tube had slots in it, there appeared streaks of light in the gas on the side away from the anode. These channels of light, first called "canal rays," were easily shown to be due to charged particles. They moved in the direction of the electric field which was producing the discharge, and they were deflected by electric and magnetic fields in directions that proved that their charge was positive. Attempts were made to measure q/m , the ratio of the charge to the mass, of these *positive rays*. It was soon discovered that q/m for positive rays was much less than for electrons and that it depended on the kind of residual gas in the tube. The velocities of these positive rays were found to be nonuniform and much less than electron velocities.

Thomson devised a different method for measuring q/m of these positive rays having nonuniform velocities. Figure 2-9 shows the apparatus he used. The main discharge took place in the large bulb A at the left, where K is the cathode and D is the anode. The gas under study was slowly admitted through the tube at L and was simultaneously pumped out at F . Thus a very low gas pressure was maintained. Most of the positive rays produced in the bulb hit the cathode and heated it. The cathode had a "canal" through it, so that some of the positive rays passed into the right half of the apparatus. Just to the right of the cathode are M and N , the poles of an electromagnet. The pole pieces of this magnet were electrically insulated by sheets, I , so that the magnetic pole pieces could also be used as the plates of a capacitor for the establishment of an electric field. With neither electric nor magnetic fields, the positive rays passed straight through the chamber C to the sensitive layer at S . This layer was either the emulsion on a photographic plate or a fluorescent screen. The beam was

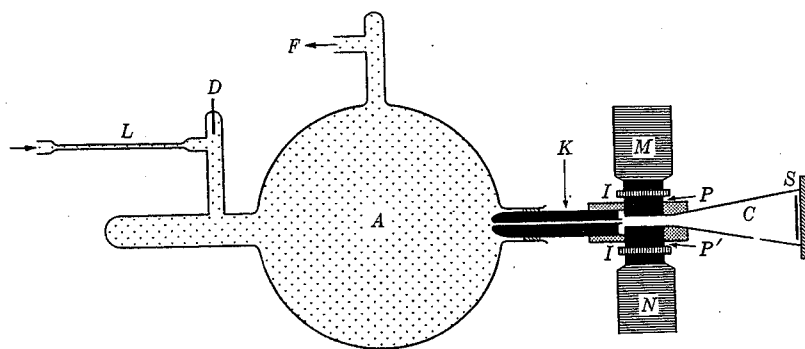


Fig. 2-9 Diagram of Thomson's apparatus for positive-ray analysis.

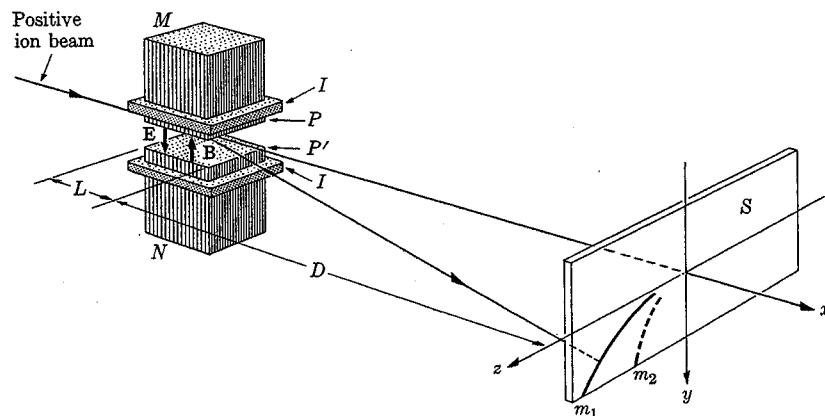


Fig. 2-10 Formation of positive-ray parabolas.

well defined because of the narrow tunnel in the cathode through which it had to pass. Instead of crossed fields as in the electron apparatus, this apparatus has its fields perpendicular to the rays but parallel to each other. The electric field is directed downward and the magnetic induction is upward, so that in Fig. 2-10 the electric force is toward the bottom of the page along the y -axis and the magnetic force is out of the page toward the reader along the z -axis.

Let a positively charged particle of unknown q/m enter the region between P and P' in Fig. 2-10 with an unknown velocity v_x along the x -axis. Then,

according to Eq. (2-12), the deflection of the particle on the screen S due to the electric field is

$$y = \frac{qEL}{mv_x^2} \left(\frac{L}{2} + D \right), \quad (2-32)$$

and, according to Eq. (2-18), the deflection at S caused by the magnetic field is

$$z = \frac{qBL}{mv_x} \left(\frac{L}{2} + D \right). \quad (2-33)$$

These two equations together are the parametric equations of a parabola, where v_x is the parameter. Since v_x is different for different particles of the same type, the pattern on the screen is not a point but a locus of points. Elimination of v_x between these equations leads to

$$z^2 = \frac{q}{m} \frac{B^2 L}{E} \left(\frac{L}{2} + D \right) y, \quad (2-34)$$

which is the equation of a parabola.

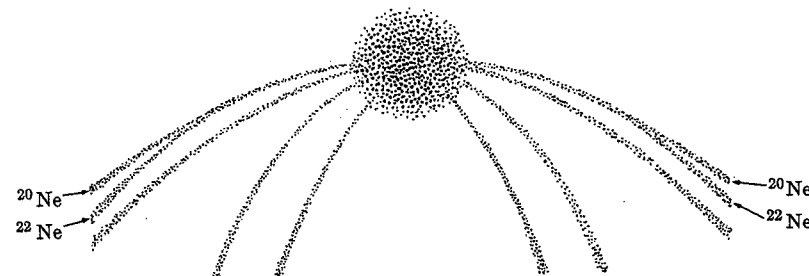


Fig. 2-11 The parabolas of neon.

Some actual parabolas obtained by Thomson's method are shown in Fig. 2-11. Examination of the figure reveals several things: Positive rays have distinct values of q/m , as is shown by the fact that the traces are clearly parabolas. That a single experiment discloses several values of q/m is evident from the fact that there are several parabolas. It is apparent that the method is not capable of great precision because the parabolas are not sharp.

Thomson assumed that each particle of the positive rays carried a charge equal and opposite to the electronic charge, and he attributed the divergent parabolas to differences in mass. He assumed that the positive rays were positive because each had lost one electron. Thomson could identify particular parabolas with particular ions (charged atoms or molecules are called *ions*). Thus for atomic hydrogen, he could verify that the q/m he measured was equal to the

value one would expect from dividing the electronic charge by the mass per atom (the atomic mass of hydrogen divided by Avogadro's number). The reason that positive rays move more slowly than electrons and have lower values of q/m than electrons is now clear: The positive rays are much more massive. The largest q/m for positive rays is that for the lightest element, hydrogen. From the value of q/m it was found that the mass of the *hydrogen ion* or *proton* is 1836.2 times the mass of an electron. Electrons contribute only a small amount to the mass of material objects.

2-7 ISOTOPES

The most striking thing that was shown by the Thomson parabolas was that certain chemically pure gases had more than one value of q/m . Most notable was the case of neon, of atomic mass 20.2. Neon exhibited a parabola situated to correspond to a particle of atomic mass 20, but it also had a parabola which indicated an atomic mass of 22. Since the next heavier element, sodium, has an atomic mass of 23.0, efforts to explain away the unexpected value of q/m failed at first. Finally, it was concluded that there must be two kinds of neon, with different masses but chemically identical. The proof of this interpretation was given by Aston, one of Thomson's students.

Aston used a principle which we discussed in Chapter 1. We pointed out there that the average kinetic energy of a molecule in a gas is $3kT/2$. Different gas molecules mixed together in a container must be at the same temperature, and hence the average kinetic energy of each kind of molecule must be the same. If the two gases have different molecular masses, the lighter molecules must have the higher average velocity, and these will make more collisions per unit time with the walls of the container than the heavier molecules. Therefore if these molecules are allowed to diffuse through a porous plug from a container into another vessel, the lighter molecules will have a higher probability of passing through than the heavier, slower ones. Aston took chemically pure neon gas and passed part of it through such a plug. Since one such pass accomplishes only a slight separation, the process had to be repeated many times. He ended with two very small amounts of gas. One fraction had been through the plug many times and the other had been "left behind" many times. He measured the atomic mass of each fraction and found values of 20.15 for the former and 20.20 for the latter. The difference was not great, but it was enough to show that there are indeed two kinds of neon (at least). Many other elements have since been shown to exist in forms that are chemically identical but different in mass. Such different forms of an element are called *isotopes* of the element. Thus Dalton's belief that all the atoms of an element were physically identical in every way was not correct.

The discovery of isotopes solved several problems. It explained the two parabolas observed by Thomson. It also gave a logical explanation of the fact

that the previously measured atomic mass of neon, 20.2, departs so far from an integral value. If chemical neon is a mixture of neon of atomic mass 20 (symbol Ne^{20}) and of neon of atomic mass 22 (Ne^{22}), then there is some proportion of the two that will mix and have an average atomic mass of 20.2.

2-8 MASS SPECTROSCOPY

A detailed search for the isotopes of all the elements required a more precise technique. Aston built the first of many instruments called mass spectrographs or mass spectrometers in 1919.* Aston introduced the idea of velocity focusing, which is explained below. His first instrument could separate ions with a difference in q/m of about 1 percent, and he could determine the magnitude of the mass to about 0.1 percent. In later work, he improved considerably upon these figures.

A modern mass spectrometer has directional focusing as well as velocity focusing. These terms can best be explained with reference to a specific instrument. As an example, Fig. 2-12 shows an instrument built by A. O. Nier and collaborators.†

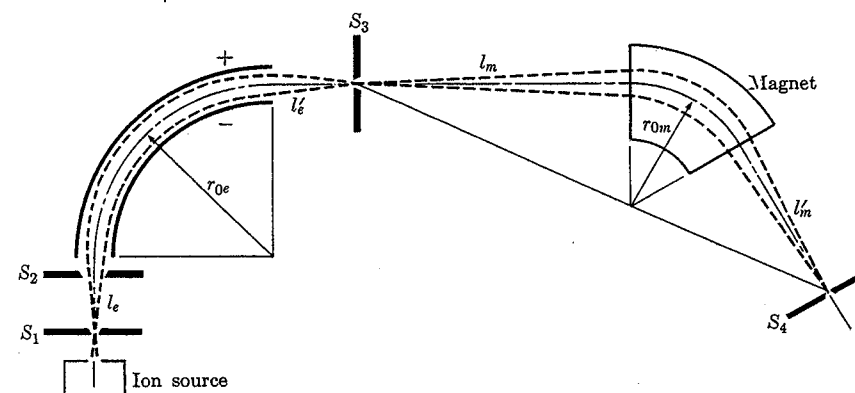


Fig. 2-12 Principle of operation of Nier's spectrograph.

Positive ions are produced in an ion source by impact from electrons emitted by an incandescent filament. The ions are accelerated through a potential difference of about 40 kV and focused by an electrostatic lens (similar to those operating in a television tube) upon slit S_1 , which is normally set to an opening of 0.0005 in. The diverging bundle of rays (particle orbits) converge after passing through an electrostatic deflector to slit S_3 and again after passing

* F. W. Aston, *Phil. Mag.* 38 (1919), p. 707.

† A. O. Nier and T. R. Roberts, *Phys. Rev.* 81 (1951), p. 507.

through a magnetic deflector to slit S_4 , behind which is a sensitive current detector (electron multiplier).

In the magnetic deflector, one can show by simple geometry why directional focusing takes place. Starting from S_3 and following the ray that goes to the left of the central ray, we see that it goes a longer distance through the magnetic field than the central ray does. It is therefore deflected through a larger angle and consequently converges with the central ray. The electrostatic deflector operates similarly, but the effect is stronger because the ray moving closest to the positive plate has higher potential energy, and therefore lower kinetic energy (inside the deflector), and is deflected more.

Directional focusing, as explained above, is vital in the operation of a mass spectrograph. Good resolving power (ability to separate different masses) can be obtained only if all particles of the same mass converge to a sharp line on slit S_4 and all particles of a different mass converge to another line spatially separated from the first.

We have assumed in the discussion of directional focusing that all particles have the same energy. This is approximately so, because they have been accelerated through the same potential (≈ 40 kV). For simplicity we assume that all have unit charge. In Aston's ion source, which was a gas-discharge tube, there was quite a difference in ion energy. In a modern spectrometer extreme care is taken to produce ions of as nearly the same energy as possible. However, with the extremely high resolving power of a modern instrument, it would still be possible to see considerable broadening of the image lines if velocity focusing were not used.

We shall not discuss the details of velocity focusing, but shall give an outline of the principle. The electrostatic deflector separates particles of different kinetic energy or mv^2 (compare Eq. 2-12). The magnetic deflector separates particles of different momenta or mv (compare Eq. 2-18). For the instrument in Fig. 2-12, the final position or point of impact of a particle on the plane of the detector slit S_4 can then be expressed as

$$\Delta y = -a \frac{\Delta(mv^2)}{m_0 v_0^2} + b \frac{\Delta(mv)}{m_0 v_0}. \quad (2-35)$$

Here $m = m_0 + \Delta m$ and $v = v_0 + \Delta v$, and a and b are constants, characteristic for the instrument. We assume that the electric and magnetic fields have been set such that a particle with mass m_0 and velocity v_0 will go through the center of S_4 ($\Delta y = 0$). The first term in Eq. (2-35) arises from the electrostatic deflector, and the second term is caused by the magnet. By partial differentiations, we get from Eq. (2-35):

$$\frac{\Delta y}{\Delta v} = -\frac{2a}{v_0} + \frac{b}{v_0}, \quad (2-36)$$

$$\frac{\Delta y}{\Delta m} = -\frac{a}{m_0} + \frac{b}{m_0}. \quad (2-37)$$

The deflecting powers (a and b) for the two deflectors are chosen such that $\Delta y/\Delta v = 0$; that is, $b = 2a$. This is the condition for velocity focusing. Clearly, the total deflecting power for a change of mass (mass dispersion) is still nonzero so that the different masses are separated.

In Fig. 2-12, slit S_2 is used to limit the angle of divergence of the bundle of rays accepted by the spectrograph, and S_3 is used to limit the range of velocities accepted for a given mass. Both slits have much wider openings than S_1 and S_4 .

With the mass spectrometer discussed above, ions with mass differences of less than one-hundredth of 1 percent ($\Delta m/m = 10^{-4}$) could be separated, and the differences could be measured to an accuracy of about one per million. Newer and larger spectrographs have since been made in which both resolving power and accuracy have been increased by almost a factor of 100.*

The atomic masses determined in a mass spectrograph are always measured relative to other ions of nearly equal mass. Since ^{12}C is the standard (see the next section), one always attempts to measure the mass difference between an unknown mass and a hydrocarbon compound of the same mass number.† This is called the *doublet method* of mass spectroscopy. An example is‡

$$^{12}\text{C} \text{H}_4 - ^{16}\text{O} = 36381.5 \pm 0.9 \mu\text{u} \text{ (micro-mass units).}$$

This is an equation with two unknowns, the mass of H^1 and the mass of O^{16} . (The mass of ^{12}C is 12.0000 by definition.) By measuring other doublets with different combinations of the same isotopes, possibly also involving others, one can determine the masses of these isotopes on the ^{12}C scale, often to within a few micro-mass units, that is, with a precision of better than one point per million.

PROBLEMS

- 2-1 What is the ratio of the electric force on a charged particle in an electric field of 20 V cm^{-1} to the force of gravity on the particle if it is a) an electron? b) a proton? c) Is the weight negligible compared with the electric force?
- 2-2 An electron moving in a vertical plane with a speed of $5.0 \times 10^7 \text{ m s}^{-1}$ enters a region where there is a uniform electric field of 20 V cm^{-1} directed upward. Find the electron's coordinates referent to the point of entry and the direction of its motion at a time $4 \times 10^{-8} \text{ s}$ later if it enters the field a) horizontally, b) at 37° above the horizontal, and c) at 37° below the horizontal.

* See, for instance, H. Matsuda, S. Fukumoto, and T. Matsuo, *Proceedings of the Third International Conference on Atomic Masses*, R. C. Barber, editor. University of Manitoba Press (1967), p. 733.

† The superscript 12 on the isotope symbol ^{12}C is the mass number, which is equal to the number of nucleons (protons and neutrons) in the nucleus. The mass number of a molecule is the sum of the mass numbers of its constituent atoms.

‡ K. S. Quisenberry, T. T. Scolman, and A. O. Nier, *Phys. Rev.* 102 (1956), p. 1071.

- 2-3 If the charged particle in Problem 2-2 were a proton instead of an electron, what must be the magnitude and direction of the electric field so that the answers for the proton would be the same as they were for the electron?
- 2-4 The dimensions of some parts of a typical commercial cathode-ray tube are given in Fig. 2-13. If electrons start from rest at the cathode, what is their velocity v_x at the origin O for an accelerating voltage of 1136 V between the anode and cathode?

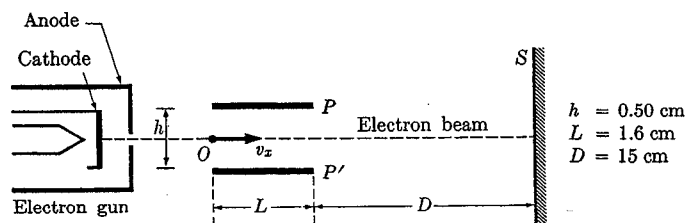


Figure 2-13

- 2-5 Given that the potential difference between the deflecting plates P and P' is 50 V in the cathode-ray tube in Problem 2-4, a) find the y -coordinate and the direction of motion of the electrons when $x = L$. b) What is the total deflection on the screen S ?
- 2-6 A large, plane metal plate is mounted horizontally at a distance of 0.80 cm above another similar horizontal plate. They are charged to a potential difference of 40 V, the upper plate being positive. An electron is projected horizontally with a velocity of 10^6 m s^{-1} from a point O which is midway between the plates. a) Find the x -coordinate of the point at which the electron strikes a plate. b) Compute the tangent of the angle that gives the direction of the electron's motion as it strikes the plate. c) What is the change in kinetic energy of the electron in going from O to the plate? d) What would the answer to part c) be if the electron had no initial velocity at O ?
- 2-7 a) Through what potential difference would a deuterium ion have to be accelerated from rest in a vacuum so that it would have a speed of $8.47 \times 10^6 \text{ m s}^{-1}$? b) What would have to be the magnitude and direction of the smallest magnetic induction that would constrain the moving deuterium ion to a circular path in an evacuated toroidal tube 1 m in diameter?
- 2-8 A uniform electric field of intensity $40 \times 10^4 \text{ V m}^{-1}$ is perpendicular to a uniform magnetic field of flux density $2 \times 10^{-2} \text{ T}$. (A tesla T is a weber per square meter, Wb m^{-2} .) An electron moving perpendicularly to both fields experiences no net force. a) Show in a diagram the relative orientation of the electric field vector, the magnetic induction vector, and the velocity of the electron. b) Calculate the speed of the electron. c) What is the radius of the electron orbit when the electric field is removed?
- 2-9 A charged particle enters the region between two very large parallel metal plates, the particle's velocity being parallel to the plates when the particle enters. The plates are separated a distance of 2 cm and the potential difference between the plates is 2000 V. When the particle has penetrated 5 cm into the space between the plates, it is found that the particle has been deflected 0.6 cm. If a perpendicular magnetic field of flux density 0.1 T is impressed simultaneously with the electric field, the particle is found to undergo no deflection at all. Calculate the charge-to-mass ratio for this particle.
- 2-10 A cathode-ray tube is placed in a uniform magnetic induction B with the axis of the tube parallel to the lines of force. Given that electrons emerging from the gun with a velocity v make an angle θ with the axis as they pass through the origin O , show a) that their trajectory is a helix, b) that they will touch the axis again at the time $t = 2m_e/Bv$, c) that the coordinate of the point touching is $x = 2m_e v \cos \theta / Be$, and d) that for small values of θ , the coordinate of the point of crossing or touching the axis is independent of θ . e) The arrangement in this problem is called a magnetic lens. Why? f) How do the trajectories of the electrons passing through the origin at an angle θ above the axis differ from those directed at an angle θ below the axis?
- 2-11 Electrons are accelerated through a potential difference of 1000 V in an electron gun and leave the narrow hole in the anode as a narrow diverging beam. What magnitude of axial magnetic induction is required to focus the beam on a screen 50 cm from the hole. (Hint: See Problem 2-10.)
- 2-12 What is the final velocity of an electron accelerated through a potential difference of 1136 V if it has an initial velocity of 10^7 m s^{-1} ?
- 2-13 Two positive ions having the same charge q but different masses, m_1 and m_2 , are accelerated horizontally from rest through a potential difference V . They then enter a region where there is a uniform electric field E directed upward. a) Show that, if the ion beam entered the field along the x -axis, then the value of the y -coordinate for each ion at any time t is $y = Ex^2/4V$. b) Can this arrangement be used for isotope separation?
- 2-14 Two positive ions having the same charge q but different masses, m_1 and m_2 , are accelerated horizontally from rest through a potential difference V . They then enter a region where there is uniform magnetic induction B normal to the plane of the motion. a) Show that, if the beam entered the magnetic field along the x -axis, the value of the y -coordinate for a small deflection of each at time t is $y = Bx^2(a/8mV)^{1/2}$. b) Can this arrangement be used for isotope separation?
- 2-15 Particles with charge q and mass m are injected into a homogeneous magnetic field having induction B . When their velocities are initially perpendicular to the field, the particles travel in circular orbits. Derive an expression for the frequency of revolution of the particles and show that the frequency is independent of the velocity.
- 2-16 A charged oil drop falls 4.0 mm in 16.0 s at constant speed in air in the absence of an electric field. The relative density of the oil is 0.80, that of the air is 1.30×10^{-3} , and the viscosity of the air is $1.81 \times 10^{-5} \text{ N s m}^{-2}$. Find a) the radius of the drop and b) the mass of the drop. c) If the drop carries one electronic

unit of charge and is in an electric field of 2000 V cm^{-1} , what is the ratio of the force of the electric field on the drop to its weight?

- 2-17 When the oil drop in Problem 2-16 was in a constant electric field of 2000 V cm^{-1} , several different times of rise over the distance of 4.0 mm were observed. The measured times were 36.1 , 11.5 , 17.4 , 7.55 , and 23.9 s . Calculate a) the velocity of fall under gravity, b) the velocity of rise in each case, and c) the sum of the velocity in part a) and each velocity in part b). d) Show that the sums in part c) are integral multiples (two significant figures) of some number and interpret this result. e) Calculate the value of the electronic charge from these data.
- 2-18 In an experiment to count and "weigh" atoms, it is found that a current of 0.800 A flowing through a copper sulfate solution for 1800 s deposits 0.473 g of copper. The atomic mass of copper is 63.54 , its valence is 2 , and the electronic charge is $1.60 \times 10^{-19} \text{ C}$. Using only the data *given in this problem*, find a) the number of electronic charges carried by the ions which deposited as copper atoms, b) the number of copper atoms deposited, c) the mass of a copper atom, d) the number of atoms in a gram-atomic mass of copper, e) the number of electronic charges carried by a gram-equivalent mass of copper ions, f) the number of Coulombs required to deposit a gram-equivalent mass of copper, and g) the mass of a hydrogen atom, given that its atomic weight is 1.008 .
- 2-19 What must be the direction of the electric field E and the magnetic induction B in Fig. 2-10 so that the segment of the positive-ion parabola will be in a) the lower right quadrant, b) the upper right quadrant, and c) the upper left quadrant, as viewed from the right of the diagram?
- 2-20 a) If the ion beam in Fig. 2-10 contains two types of ions having equal charges but different masses, which of the two parabolic segments will have those of greater mass? b) If the masses are equal but the charges different, which segment will contain those having the larger charge?
- 2-21 For a particular parabola in Thomson's mass spectrograms, what physical quantity is different for the ions that land close to the origin than for those landing farther away? Why does this difference exist, in spite of the fact that a constant voltage was used for the gas discharge?
- 2-22 In a mass spectrometer, ions having the same charge q but different masses m_1 and m_2 are accelerated from rest through a potential difference V . A narrow beam of these ions then enters a magnetic field having a magnetic induction B which is perpendicular to the motion of the particles. Derive a simple expression in terms of the *given* quantities for the *ratio* of the radii of the trajectories of the two types of ions in the magnetic field.
- 2-23 Copper has two isotopes whose masses are 62.9 and 64.9 , respectively. What is the percent of abundance of each in ordinary copper having an atomic mass of 63.5 ?
- 2-24 Uranium hexafluoride, UF_6 , is a gaseous compound at 100°C . Given a mixture of two such hexafluorides, one of the isotope ^{235}U and the other of ^{238}U , find the root-mean-square speed of each molecule. Comment on the possibility of separating these by a diffusion process.

The Atomic View of Radiation

3-1 INTRODUCTION

All sources of light consist of matter which is excited in one way or another. The firefly excites his body matter by some obscure chemical process; the matter of the sun is excited by heat. But ever since Heinrich Hertz demonstrated the validity of Maxwell's theory of electromagnetic radiation, we have known that the ultimate source of radiation is an accelerated electric charge. We cannot begin the story of radiation with Maxwell, however, if we are to appreciate one of the most dramatic demonstrations of the scientific method.

3-2 PARTICLES OR WAVES

Certain Greeks of ancient times argued that since a blind man reaches out to feel his way about, the seeing man must reach out with his eyes. They thought of light as a kind of tentacle emitted by the eye yet retaining contact with the eye so that information about objects touched was conveyed to the mind. Such a view obviously fails to explain why a man cannot see at night unless there is an outside source of illumination.

It was realized long ago that light consists of something which goes out from certain "sources," bounces off objects, and may finally enter the eye. In the seventeenth century there were two views on the nature of the "something" that was bouncing about. Newton defended the premise that light consists of a stream of fast-moving elastic particles of very small mass. His view accounted for the law of reflection, which states that the angle of incidence is equal to the angle of reflection. (This is the way perfectly elastic balls bounce from the sidewalk.) He accounted for the law of refraction by arguing that when particles of light are very near any optically dense medium like glass, they are attracted to it, and this attraction increases the component of the velocity of light in a direction perpendicular to the surface. Thus, according to Newton,

the light travels through the medium *faster* than it does in free space and has its direction altered *toward* the normal. Christian Huygens, on the other hand, supported the view that light consists of waves. The most impressive argument in his favor at that time was that two light beams can cross through each other without "colliding." He too explained reflection and refraction. His explanation of refraction was that when a wave front penetrates an optically dense medium at an angle, the wave moves more *slowly*. This slowing of the wave front causes the wave's direction of advance to be altered *toward* the normal.

3-3 ELECTRICITY AND LIGHT

After a century of neglect, the undulatory theory of light was revived by the versatile English scientist Thomas Young. In 1801, he showed that only the principle of interference of waves could explain the colors of thin films and of striated surfaces. During the next half century, further experimental work, especially by the French physicists Fresnel, Arago, Malus, Cornu, Fizeau, and Foucault, showed that the particle theory of light was not tenable. This work reached its culmination in 1864 when James Clerk Maxwell announced the results of his efforts to put the laws of electricity into good mathematical form. He had succeeded in this formulation and found in addition an important by-product: the laws could be combined into the mathematical form of the wave equation for electromagnetic waves. He showed, furthermore, that the velocity of these waves is the *velocity of light*! Thus in one dramatic move he put the theory of electricity in order and incorporated all optics into that theory.

Huygens' view completely displaced Newton's when Foucault found the velocity of light in an optically dense medium *less* than its velocity in free space, and Maxwell's theory was verified in 1888 when Hertz demonstrated that oscillating currents in an electric circuit can radiate energy through space to another similar circuit. Hertz used a circuit containing inductance and capacitance, hence capable of oscillating. Whenever a spark jumped across a gap in the active (transmitting) circuit, electromagnetic waves were radiated from the region in which the electric discharge occurred. (Modifications of this first transmitter were used for radio communication until the advent of vacuum tubes.) The passive or receiving circuit was a loop of wire containing a gap. When energy was transferred from one circuit to the other, sparks jumped across the receiver gap. Hertz's experiments showed that the radiation generated by electric circuits obeyed the known laws of optics. It thus appeared that the theory of light was in a satisfactory and elegant state.

Yet the last word on this subject had not been said. Hertz noted that the induced spark was more easily produced when the terminals of the receiving gap were illuminated by light from the sparks in the transmitter gap. This effect was studied more fully by one of Hertz's students, Hallwachs, who

showed that a negatively charged clean plate of zinc loses its charge when illuminated by ultraviolet light. Thus Hertz's verification of Maxwell's wave theory of light led almost simultaneously to the discovery of the photoelectric effect which, as we shall see, led in turn to a profound reinterpretation of the wave theory of radiation.

3-4 ELECTRODYNAMICS

Maxwell's equations and the theory of propagation of electromagnetic waves are given in all texts on electricity and magnetism and will not be treated in detail here. A brief review is in order, however.

Consider a charged particle executing sinusoidal motion with angular frequency ω , for instance, by being forced to move up and down in a vertical antenna. The charge produces an electric field, $E = q/4\pi\epsilon_0 r^2$, which can be measured near the antenna, but because of the r^{-2} dependence, diminishes rapidly as the distance increases. In addition to this electrostatic near field, the oscillating particle produces an electromagnetic field, the magnitude of which decreases only as r^{-1} . This field moves as a wave with a velocity which in free space is $c = (\epsilon_0\mu_0)^{-1/2}$. Here $\epsilon_0 = 8.85415 \times 10^{-12} \text{ Fm}^{-1}$ is the permittivity of free space and $\mu_0 = 4\pi \times 10^{-7} \text{ Hm}^{-1}$ is the permeability of free space. This wave moves out from the antenna in all directions but with an intensity that varies from zero in the direction of the antenna to maximum in the direction perpendicular to the antenna.

The electric and magnetic field intensities in the electromagnetic wave are perpendicular to each other, and both are perpendicular to the direction of propagation of the wave. This is illustrated in Fig. 3-1, in which the source, the antenna, is to the far left in the xy -plane and is centered on the x -axis.

In considering atomic radiations, we replace the antenna currents with electrons revolving in atomic orbits. However, as we shall see later, the classical theory of radiation has to be modified in the atomic case.

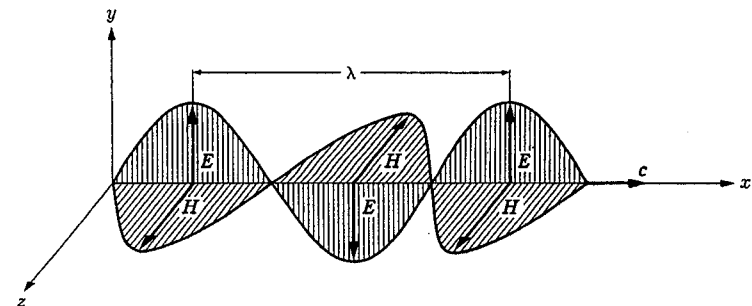


Fig. 3-1 A plane-polarized electromagnetic wave of wavelength λ showing the relation of the vectors E , H , and c .

The energy transmitted by the electromagnetic waves in a radiation field may be specified either in terms of the intensity or of the energy density of the wave motion. The intensity of the radiation is defined as the energy transmitted in unit time through a unit area normal to the direction of propagation of the waves. This is Poynting's vector. The MKSA unit of intensity is watts per square meter. The *energy density* or volume density of the radiation is defined as the amount of radiant energy in a unit volume of space. The MKSA unit of energy density is joules per cubic meter. It is evident that the energy density is equal to the intensity divided by the velocity of propagation of the wave. The term *energy density* is particularly useful in discussing the radiation within a heated enclosure.

3-5 THE UNITY OF RADIATION

From previous studies, the readers of this book are aware that the many forms of radiation, heat, light, radar, radio, etc., differ from one another in frequency

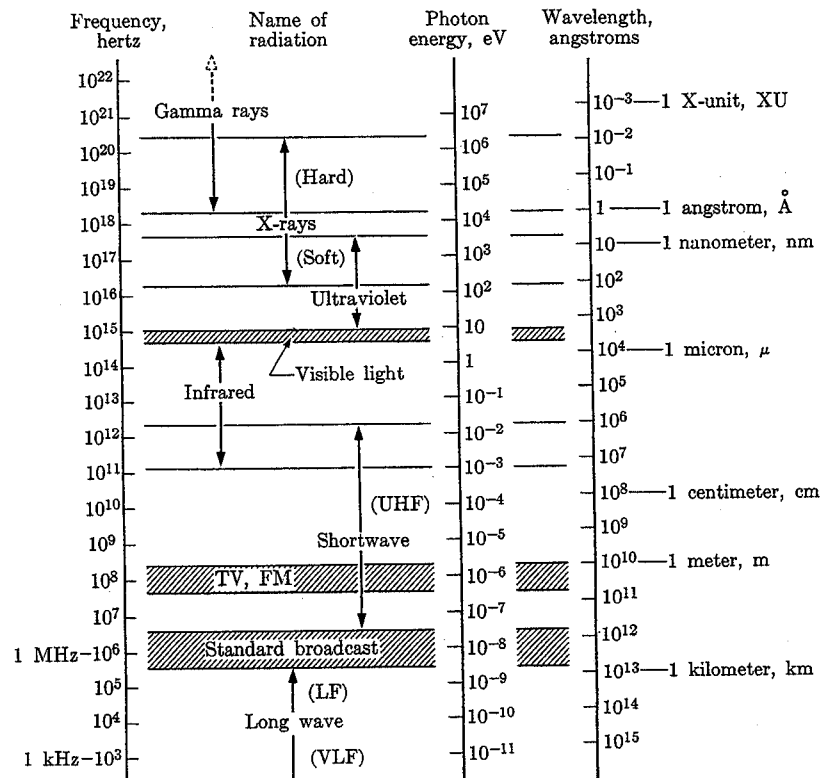


Fig. 3-2 The spectrum of electromagnetic radiation.

but not in kind. The so-called "kinds" of radiation are characterized by the techniques used to produce and detect them; actually, they all travel through free space with the same velocity and should all be understood in terms of the same theory. The tremendous range of the electromagnetic spectrum is shown in Fig. 3-2 (photon energy, mentioned in the figure, will be discussed later in this chapter). The classical theory of Maxwell applies to all these radiations and all are due ultimately to the acceleration of electrical charges. Except for differences of frequency, an observation made on one "kind" of radiation must also be true of all other kinds.

3-6 THERMAL RADIATION

Information about the nature of all radiation may be obtained from a study of any of the "kinds" of radiation. We now consider the radiation from heated bodies, since that investigation has proved particularly fruitful. We all know that a body will emit visible radiation if it is hot enough. A close relation between temperature and radiation is further implied by the fact that a white-hot body is hotter than a red-hot one. We might explore this matter further by passing the radiation from a hot body through some dispersive instrument such as a prism or grating spectrometer. If we measure the radiant energy emitted by a hot body (No. 1) for a whole series of radiant frequencies, we might obtain a graph similar to the dashed curve in Fig. 3-3. The ordinate of this curve is called the *monochromatic emittance*, W_λ , which is the amount of energy radiated per unit time per unit area of emitter in a wavelength range $d\lambda$; the abscissa is the wavelength rather than the frequency. Repeating the same experiment for another body (No. 2) of a different material but at the same temperature, we might now obtain the dotted curve of Fig. 3-3. It is clear from the figure that at most wavelengths the first body is a more efficient emitter at the given temperature than the second. Although the two curves differ, they have the same general character. They come to their highest points at about

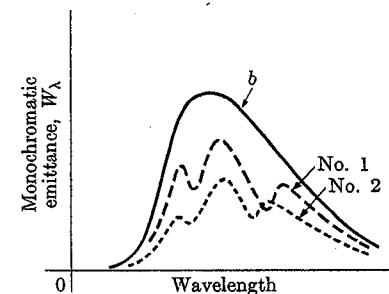


Fig. 3-3 The radiation spectrum of several hot bodies.

the same wavelength. Upon studying a great variety of substances all at the same temperature, we would obtain a great variety of emission curves, but none of these would ever have a greater monochromatic emittance, $W_{\lambda b}$, than the envelope curve, shown as a solid line in Fig. 3-3. It appears that this curve may have a significance which does not depend on the nature of the emitting material. Let us attempt to find or make an emitter which has an emission curve identical to the solid curve of Fig. 3-3.

3-7 EMISSION AND ABSORPTION OF RADIATION

It may be wondered why it is, if the surfaces of all bodies are continually emitting radiant energy, that all bodies do not eventually radiate away all their internal energy and cool down to a temperature of absolute zero. The answer is that they would do so if energy were not supplied to them in some way. In the case of the filament of an electric lamp, energy is supplied electrically to make up for the energy radiated. As soon as this energy supply is cut off, these bodies do, in fact, cool down very quickly to room temperature. The reason that they do not cool further is that their surroundings (the walls, and other objects in the room) are also radiating, and some of this radiant energy is intercepted, absorbed, and converted into internal energy. The same thing is true of all other objects in the room—each is both emitting and absorbing radiant energy simultaneously. If any object is hotter than its surroundings, its rate of emission will exceed its rate of absorption. There will thus be a net loss of energy and the body will cool down unless heated by some other method. If a body is at a lower temperature than its surroundings, its rate of absorption will be larger than its rate of emission and its temperature will rise. When the body is at the same temperature as its surroundings, the two rates become equal, there is no net gain or loss of energy, and no change in temperature.

Figure 3-3 shows that the emittance of a surface W is different at different wavelengths and the paragraph above implies that it is greater for higher temperatures. To simplify our next discussion consider an infinitesimal band of wavelengths and several opaque bodies in thermal equilibrium with each other and their surroundings. Because the bodies are opaque they will not transmit radiation and therefore, in general, part of the incident radiation will be reflected and the remainder will be absorbed. The fraction absorbed, called the *absorptance* a , plus the fraction reflected, called the *reflectance* r , must be unity or, since the surfaces may be different,

$$a_1 + r_1 = 1, \quad a_2 + r_2 = 1, \quad \text{etc.} \quad (3-1)$$

Since the bodies are in thermal equilibrium with their surroundings, they will be "bathed" in radiation of uniform intensity, I . If this is not obvious, it may be helpful to think of the bodies as being tiny specks near each other but too small to cast shadows on each other. We can now write the last sentence

quantitatively. The total radiation in a time Δt from body No. 1, which has an area ΔA_1 and a radiant emittance W_1 , is $W_1 \Delta A_1 \Delta t$. The absorption by the same body in the same time is $a_1 I \Delta A_1 \Delta t$. For the condition of thermal equilibrium to exist these must be equal. Therefore we have

$$W_1 \Delta A_1 \Delta t = a_1 I \Delta A_1 \Delta t, \quad (3-2)$$

and similarly for another body,

$$W_2 \Delta A_2 \Delta t = a_2 I \Delta A_2 \Delta t, \quad \text{etc.} \quad (3-3)$$

Dividing Eq. (3-2) by Eq. (3-3), we obtain

$$\frac{W_1}{W_2} = \frac{a_1}{a_2} \quad \text{or} \quad \frac{W_1}{a_1} = \frac{W_2}{a_2}, \quad \text{etc.} \quad (3-4)$$

Since the number of specks or kinds of surface has not been restricted, it becomes evident that W/a for any substance must be a constant (which may, of course, still depend on wavelength and temperature).

We have just proved that a body or surface which is a good emitter (high value of W) must be a good absorber (high value of a) and conversely. If we could find a perfect absorber, we would necessarily have found the best possible emitter, the graph of which is shown as b in Fig. 3-3.

3-8 BLACK-BODY RADIATION

In acoustics, an open window is taken to be a perfect absorber of sound, since an open window reflects virtually no sound back into the room. In optics, there are few things darker than the keyhole of a windowless closet, since what little light gets into the closet bounces around against absorbing surfaces before it is redirected out the keyhole. Painting the inside of the closet black may increase the darkness of the keyhole, but the essential darkness of the hole is due to the geometry of the cavity rather than to the absorptivity of its surfaces. A small hole in a cavity of opaque material is the most perfect absorber of radiant energy man has found. Conversely, a small hole in a cavity is the most perfect emitter man has devised. We can conclude this from the proof above or we can understand it more thoroughly from the following. If we look into a hole in a heated cavity, we can see the radiation from the inside wall just opposite to the hole. In addition, we see some radiation from other parts of the inside of the cavity which was directed toward the spot of wall we are looking at and is reflected to us by that spot. The absorption and emission of radiation by a hole in a hollow tungsten cylinder is shown in Fig. 3-4. The light streak across the center of the figure is an incandescent filament maintained at a constant color temperature for comparison purposes. When the cylinder is cold, the hole is darker than any other part and actually appears black, but when the cylinder is heated sufficiently, the hole is brighter than the body of

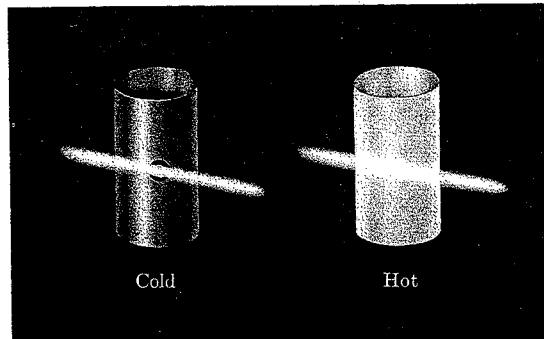


Fig. 3-4 Radiation from a hollow tungsten cylinder.

the tube and matches the reference filament. Such a hollow absorber-emitter is called a black body. Since a is equal to unity for black body, from Eq. (3-4) we obtain

$$\frac{W_1}{a_1} = \frac{W_2}{a_2} = \frac{W_b}{1} = W_b. \quad (3-5)$$

This relation is called Kirchhoff's law of radiation: *The ratio of the radiant emittance of a surface to its absorptance is the same for all surfaces at a given temperature and is equal to the radiant emittance of a black body at the same temperature.*

We now discuss the multiple-reflection situation of a radiant cavity quantitatively. Consider the radiation traveling back and forth in an isothermal cavity formed between two plane parallel sheets of different materials, as shown in Fig. 3-5. Let us now follow the history of the radiation emitted from a unit

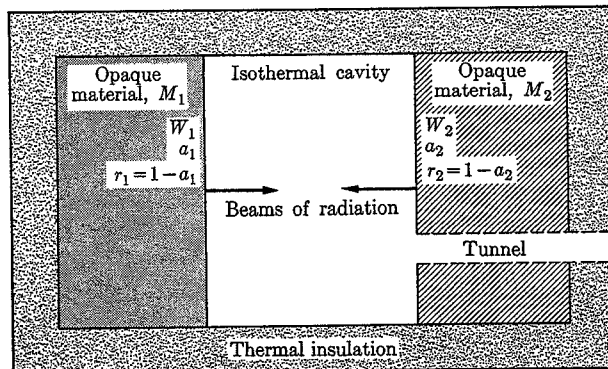


Fig. 3-5 Radiation traveling between two different materials.

area of each face in a time interval Δt , which is just long enough to permit the radiation to travel across the space to the other face. It is reflected there with some loss of energy, returns to the first face, is reflected there with further loss, and so on. Table 3-1 gives the values and the direction of travel of the com-

Table 3-1

Initially emitted by M_1	Initially emitted by M_2
$\rightarrow W_1 \Delta t$	$\leftarrow W_2 \Delta t$
$\leftarrow (1 - a_2)W_1 \Delta t$	$\rightarrow (1 - a_1)W_2 \Delta t$
$\rightarrow (1 - a_1)(1 - a_2)W_1 \Delta t$	$\leftarrow (1 - a_1)(1 - a_2)W_2 \Delta t$
$\leftarrow (1 - a_1)(1 - a_2)^2 W_1 \Delta t$	$\rightarrow (1 - a_1)^2(1 - a_2)W_2 \Delta t$
$\rightarrow (1 - a_1)^2(1 - a_2)^2 W_1 \Delta t$	$\leftarrow (1 - a_1)^2(1 - a_2)^2 W_2 \Delta t$
$\leftarrow (1 - a_1)^2(1 - a_2)^3 W_1 \Delta t$	$\rightarrow (1 - a_1)^3(1 - a_2)^2 W_2 \Delta t$
$+\dots$	$+\dots$

ponents in the radiation streams per unit area between the walls after several intervals of Δt have elapsed.

While these successive traverses of the initial radiation from each face are occurring, both faces continue to emit. Therefore, when the steady state has been reached, there are simultaneous columns of thermal radiation going back and forth in the space between the faces. The total radiation streaming in one direction, say to the right, is simply the sum of all the components in the direction \rightarrow . Therefore, the total effective emittance toward the right is given by

$$\begin{aligned} W_r \Delta t = & W_1 \Delta t + (1 - a_1)(1 - a_2)W_1 \Delta t + (1 - a_1)^2(1 - a_2)^2 W_1 \Delta t \\ & + \dots + (1 - a_1)W_2 \Delta t + (1 - a_1)^2(1 - a_2)W_2 \Delta t \\ & + (1 - a_1)^3(1 - a_2)^2 \Delta t + \dots \end{aligned} \quad (3-6)$$

Let $x = (1 - a_1)(1 - a_2)$. Then substituting this in the preceding equation we obtain

$$W_r = W_1[1 + x + x^2 + \dots] + W_2(1 - a_1)[1 + x + x^2 + \dots]. \quad (3-7)$$

The series within the pairs of brackets is a simple geometric progression whose limit, since $0 < x < 1$, is $1/(1 - x)$. In terms of the absorptances, this limit is

$$\begin{aligned} \frac{1}{1 - x} &= \frac{1}{1 - (1 - a_1)(1 - a_2)} = \frac{1}{1 - (1 - a_1 - a_2 + a_1 a_2)} \\ &= \frac{1}{a_1 + a_2 - a_1 a_2}. \end{aligned} \quad (3-8)$$

Because the system is isothermal, we can obtain the following relations from Kirchhoff's radiation law (Eq. 3-5):

$$W_1 = a_1 W_b \quad \text{and} \quad W_2 = a_2 W_b. \quad (3-9)$$

Substituting the values from Eq. (3-8) and Eq. (3-9) in Eq. (3-7), we have

$$W_r = \frac{a_1 W_b + a_2 W_b(1 - a_1)}{a_1 + a_2 - a_1 a_2} = \frac{W_b(a_1 + a_2 - a_1 a_2)}{a_1 + a_2 - a_1 a_2} = W_b. \quad (3-10)$$

This equation shows that the radiation to the right (it could just as well have been in any other direction) is effectively radiated from the left surface as though from a black body. If a tunnel, which is so small it does not subtract a significant portion of the radiation in the cavity, is bored through the right-hand face, then *the leakage radiation will be black body-radiation*. It is to be noted that the derivation contained no assumptions about either the nature of thermal radiation or of the kinds of surfaces inside the enclosure.

We now know how to make a black body and have achieved the goal we set at the end of Section 3-6.

The reader can demonstrate for himself that black bodies can even be made from bright objects. A bundle of sewing needles held with their points directed toward the eye looks remarkably black. A pile of razor blades at least $\frac{1}{16}$ -inch thick also looks black when viewed from the sharp side. In these cases the incident radiation is completely absorbed as a result of all the partial absorptions experienced at the many successive partial reflections it undergoes in traveling down into the relatively deep, narrow spaces between the needles or the blades.

We now return to the question of the spectrum of the radiation emitted by a hot body. If we take a black body as our sample, we can measure the emission from the hole as we did the material samples in getting the data for Fig. 3-3. This experiment shows that the emission of the black body gives at once the smooth solid curve of Fig. 3-3, which, unlike the other curves in the figure, is independent of the material used to make the emitter. This confirms what we might have suspected before, that the solid curve portrays a general characteristic of thermal radiation at a given temperature. A study of this curve should give information about radiation itself. With consideration of the material composing the cavity eliminated, the remaining important variable is the temperature of the radiation source. Mathematically, the total energy radiated per unit time per unit area of emitter is proportional to the area under the curve, and Stefan found empirically that this area is directly proportional to the fourth power of the absolute temperature,

$$W_b = \sigma T^4, \quad (3-11)$$

where σ is called the *Stefan-Boltzmann's constant*. Its value is

$$\sigma = (5.6696 \pm 0.0010) \times 10^{-8} \text{ W} \cdot \text{m}^{-2} \cdot ^\circ\text{K}^{-4}.$$

Equation (3-11) was first derived theoretically by Boltzmann and is therefore called Stefan-Boltzmann's law. In the following two sections, we shall derive the equation giving the spectral distribution of black-body radiation (Planck's law). Equation (3-11) can then be found by integration (Problem 3-5). Boltzmann derived the law by a thermodynamic argument* before Planck's work.

A body that is not black will radiate less energy than the black body. Combining Eqs. (3-5) and (3-11), we get, in general,

$$W = a\sigma T^4. \quad (3-12)$$

The coefficient a , called *total emissivity* or absorptance, is tabulated in all standard handbooks of physics.

The thermodynamic method employed by Boltzmann can be pushed a little further in predicting properties of the spectral distribution of black-body radiation. Wien found that as the temperature of any black body is changed the curve retains its general shape, but that the maximum of the curve shifts with temperature so that the wavelength of the most intense radiation is inversely proportional to the absolute temperature, or $\lambda_{\text{max}} = \text{const}/T$. This is a special case of *Wien's displacement law*, which states that at corresponding wavelengths the monochromatic energy density of the radiation in the cavity of a black body varies directly as the fifth power of the absolute temperature. The relation defining corresponding wavelengths at temperatures T_1 and T_2 is $\lambda_1 T_1 = \lambda_2 T_2$. The displacement law enables us to predict the entire curve at *any* temperature, given the entire curve at *one* particular temperature. Neither of these radiation laws, however, treats the basic problem of why the energy radiated from a black body has this particular wavelength distribution.

3-9 WIEN AND RAYLEIGH-JEANS' LAWS

A comparison of the experimental black-body radiation curves of Fig. 3-6 and the Maxwell distribution of speeds in a gas shown in Fig. 1-2 shows a remarkable similarity. Wien noted this similarity and tried to fit a function such as Maxwell had derived for the speed distribution to the black-body wavelength distribution. There is more than the similarity of the curves to justify this approach. If the molecules of the black body are thermally agitated, then their distribution of speeds may be somewhat like that derived by Maxwell. The accelerations of these molecules should be related to their velocities. These molecules contain charges which are therefore thermally accelerated, and we have shown that classical electrodynamics indicates that radiation results from accelerated charges. This argument is hardly rigorous, but it is a plausible explanation of the relationship between the similar curves. The expression that Wien obtained

* See, for instance, F. K. Richtmyer, E. H. Kennard, and T. Lauritsen, *Introduction to Modern Physics*. New York: McGraw-Hill, (1955).

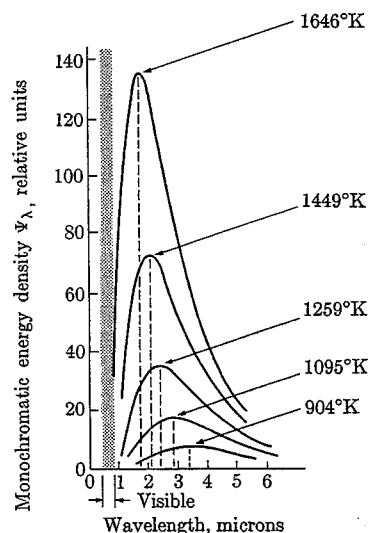


Fig. 3-6 The distribution of energy in the spectrum of the radiation from a black body at different temperatures.

for the monochromatic energy density ψ_λ within an isothermal black-body enclosure in the wavelength range λ to $\lambda + d\lambda$ is

$$\psi_\lambda d\lambda = \frac{c_1 \lambda^{-5}}{e^{c_2/\lambda T}} d\lambda, \quad (3-13)$$

where λ is the wavelength, T is the absolute temperature, and e is the base of natural logarithms. This formula is essentially empirical and contains two adjustment constants c_1 and c_2 , called the first and second radiation constants, respectively. Wien chose these constants so that the fit he obtained was rather good except at long wavelengths. The graph of Wien's law is shown dashed in Fig. 3-7. The points represent the experimental data of Lummer and Pringsheim.* But a "pretty good fit" is not good enough, and a formula which is essentially empirical tells us nothing about the nature of radiation.

Lord Rayleigh set out to derive the radiation distribution law in a rigorous way. He argued that the law of equipartition of energies (Section 1-8) should apply to the electromagnetic field in an enclosure. A standing wave of a given frequency interacts with oscillating atoms in the wall. Energy can flow in either direction from the wall to the field or conversely. The "temperature" of the field is therefore the same as the temperature of the walls. A one-dimensional harmonic oscillator has one degree of freedom representing its

* Lummer and Pringsheim, *Verhandl. Deut. Physik. Ges.* 1 (1899), pp. 23 and 215; 2 (1900), p. 163.

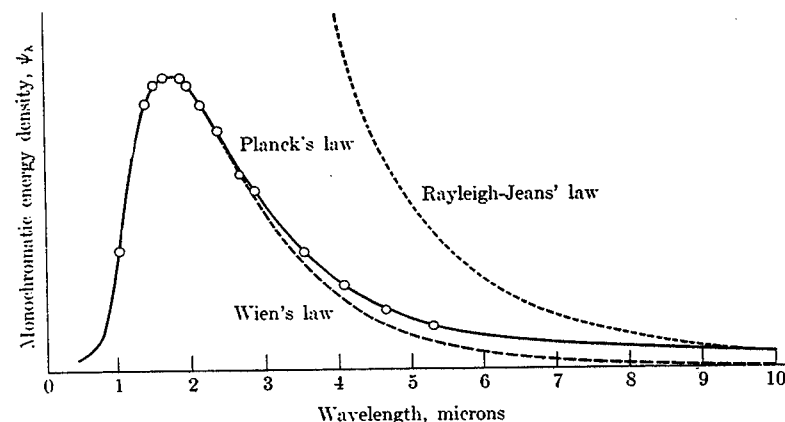


Fig. 3-7 Graphs of the radiation laws. Points represent experimental data.

kinetic energy, and, since the average potential energy equals its average kinetic energy ($\frac{1}{2}kT$), the total average energy is kT . A standing wave of electromagnetic radiation with a given direction of polarization represents a one-dimensional oscillator and should therefore have an average energy of kT . This is the basis for the derivation of Rayleigh-Jeans' radiation law. The law gives the energy content in an isothermal enclosure in a wavelength interval λ to $\lambda + d\lambda$. To derive it, we need to know how many *different* standing waves, called *modes* of radiation, there are in this wavelength interval. Each mode is then assumed to have an average energy of kT .

Let us first look at the simpler problem of calculating the number of modes of oscillations in a given frequency interval on a vibrating string. The x -axis is along the string, which is clamped at $x = 0$ and $x = L$. We know from mechanics that standing transverse waves can be expressed as

$$y = A \sin kx \sin \omega t, \quad (3-14)$$

with

$$kL = n\pi, \quad (3-15)$$

where n is a positive integer. The *wave number* k , the wavelength λ , the angular frequency ω , the frequency ν , and the wave velocity c on the string are related by the following equations:

$$k = 2\pi/\lambda, \quad \omega = 2\pi\nu, \quad c = \omega/k = \lambda\nu. \quad (3-16)$$

A mode of oscillation is by definition a standing wave with a given value of n . Our objective now is to count the number of possible values of n in a given frequency interval. We simply differentiate Eq. (3-15) and find

$$dn = \frac{L}{\pi} dk = \frac{L}{\pi c} d\omega. \quad (3-17)$$

By substituting $dk = -(2\pi/\lambda^2) d\lambda$ and neglecting the minus sign, we can also write

$$dn = \frac{2L}{\lambda^2} d\lambda. \quad (3-18)$$

For example, if the string is $L = 100$ cm, Eq. (3-18) states that there can be 20 standing waves of different wavelengths in the interval $\lambda = 1$ cm to $\lambda + d\lambda = 1.1$ cm.

Let us now attack the three-dimensional problem, which, in principle, is very like the one we have discussed. We shall assume that the walls are perfectly reflective. If this were strictly true, there would be no exchange of energy between the wall and the electromagnetic field. However, we can imagine that the walls are almost perfectly reflective, and this modification will not change our calculation of the number of modes. Assume that the cavity is cubical with sides L . We can then find solutions of Maxwell's equation of the form

$$E_x = E_0 \cos k_x x \sin k_y y \sin k_z z \sin \omega t, \quad (3-19)$$

with

$$\omega = c(k_x^2 + k_y^2 + k_z^2)^{1/2}. \quad (3-20)$$

The expressions for E_y , E_z , H_x , H_y , and H_z are similar to Eq. (3-19). This is the three-dimensional version of Eq. (3-14). The x -dependence is a cosine function in Eq. (3-19) but will be a sine function with the same wave number k_x in the expression for E_y and E_z . The boundary conditions are now such that the components of the E -vector parallel to a given surface must be zero at that surface. This gives

$$\begin{aligned} k_x L &= n_x \pi, \\ k_y L &= n_y \pi, \\ k_z L &= n_z \pi, \end{aligned} \quad (3-21)$$

where n_x , n_y , and n_z are positive integers. Combined with Eq. (3-20), this gives

$$\omega = \frac{\pi c}{L} (n_x^2 + n_y^2 + n_z^2)^{1/2}. \quad (3-22)$$

A given set of integral values of n_x , n_y , and n_z represents a mode of electromagnetic oscillation with a given set of node planes. Another set of integers n_x , n_y , n_z corresponds to a different set of node planes. For each set there can be two independent directions of polarization. There are therefore two independent modes for each set n_x , n_y , and n_z .

We now ask how many different sets of n_x , n_y , and n_z result in an angular frequency below a given value ω (Eq. 3-22). The answer can be found most easily by plotting in a cartesian coordinate system the values of n_x , n_y , and n_z

along the three axes (Fig. 3-8). Each volume element in the first quadrant of this coordinate system contains one point corresponding to two modes of electromagnetic radiation. The positive numbers n_x , n_y , and n_z are components of a vector n , the maximum length of which is limited when there is a limit for the angular frequency ω . The relationship between the two is given by Eq. (3-22) as

$$n_{\max} = \omega L / \pi c. \quad (3-23)$$

The total number of points, each of which represents two modes of radiation, can then be found by counting the number of unit volumes in the first quadrant within the distance n_{\max} from the origin. This is equal to one-eighth the volume

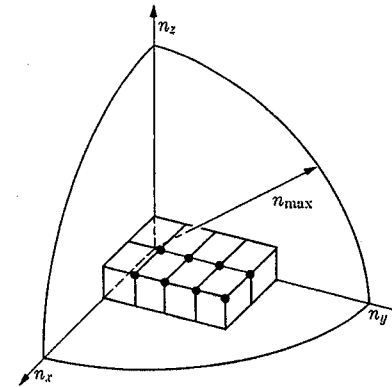


Fig. 3-8 Each point in this diagram represents a possible set of integers n_x , n_y , and n_z .

of a sphere with radius n_{\max} . The number of states with angular frequency lower than ω is therefore

$$N = 2 \frac{1}{8} \frac{4}{3} \pi \left(\frac{\omega L}{\pi c} \right)^3 = \frac{\omega^3 V}{3\pi^2 c^3} = \frac{8\pi V}{3\lambda^3}, \quad (3-24)$$

where $V = L^3$ is the volume of the box. The number of modes in the wavelength interval between λ and $\lambda + d\lambda$ is found by differentiation. Neglecting the minus sign, we find that

$$dN = \frac{8\pi V}{\lambda^4} d\lambda. \quad (3-25)$$

The energy density is now simply the number of modes per unit volume multiplied by kT :

$$\psi_\lambda d\lambda = \frac{8\pi kT}{\lambda^4} d\lambda. \quad (3-26)$$

This is Rayleigh-Jeans' law, which is plotted in Fig. 3-7 for comparison with the experimental data. At first glance this law appears vastly inferior to Wien's. Although it fits well for long wavelengths, at short wavelengths or high frequencies it heads toward infinity in what has been dramatically called the "ultraviolet catastrophe." Theoretically, however, the Rayleigh law must be taken far more seriously than Wien's. It was derived rigorously on the basis of classical physics. It involves no arbitrary constants, and where it does fit the experimental curve, it fits exactly. Whereas the failure of the Wien law was "too bad," the failure of the Rayleigh law presented a crisis. It indicated that classical theory was unable to account for an important experimental observation. This was the situation to which Max Planck directed himself.

3-10 PLANCK'S LAW; EMISSION QUANTIZED

Planck's first step was essentially empirical. He found that by changing Wien's formula slightly to

$$\psi_\lambda d\lambda = \frac{c_1 \lambda^{-5}}{e^{c_2/kT} - 1} d\lambda, \quad (3-27)$$

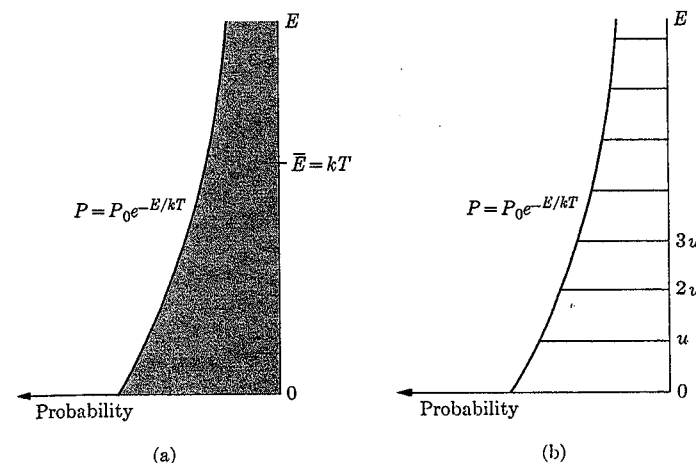
and by adjusting Wien's constants, he got a formula that reduced to the Rayleigh formula at long wavelengths and that fitted the experimental curve everywhere. He knew that he had found a correct formula and that it ought to be derivable. Planck's position was a little like that of a student who has peeked at the answer in the back of the book and is now faced with the task of showing how that answer can be logically computed. Planck tried by every method he could conceive to derive this correct formula from classical physics. He was finally forced to conclude that there was no flaw in Rayleigh's derivation and that the flaw must lie in classical theory itself.

Planck had to eliminate the "ultraviolet catastrophe" which came into Rayleigh's derivation because of the assumption that the radiation standing waves had an infinite number of modes of vibration (Eq. 3-24 with $\lambda \rightarrow 0$). Each of these was assumed to have an average energy kT and therefore the total energy content of the radiation field would be infinite. This is clearly unreasonable. Perhaps the high-frequency modes are not excited, or are they harder to excite? Let us take another look at the assumption of equipartition.

In effect, Rayleigh assumed that the energy content in one mode of oscillation could have any value from zero up and that the probability of finding an oscillator with energy E is given by Boltzmann's formula (Eq. 1-44). This gives an average energy

$$\bar{E} = \frac{\int E e^{-E/kT} dE}{\int e^{-E/kT} dE} = kT. \quad (3-28)$$

Another way of expressing this is to say that the modes can be in different *energy states*. Rayleigh assumed a continuum of states with a population proportional to the probability given by Boltzmann's law (see Fig. 3-9a).



Figs. 3-9a and 3-9b (a) Probability P of finding an energy content E in a given mode of oscillation according to classical theory (Rayleigh). (b) Same as (a), but energy content can only take on discrete values, $E = mu$ (Planck). As drawn, this is an *energy-level diagram* with the horizontal coordinate indicating *relative population* in each level.

Planck postulated that each mode could only receive energy from the walls in discrete steps u . The energy content of one mode would then be $0, u, 2u, 3u$, etc., or in general mu , where m is an integer. Let us see what this line of reasoning leads to. (The method at this point is following a procedure used by Boltzmann in 1877 to determine the distribution of kinetic energy among the molecules in a gas.) The number of oscillators having the energy m_u is

$$n_m = n_0 e^{-mu/kT}. \quad (3-29)$$

The energy contributed by the n_m oscillators is obviously

$$mun_m = mun_0 e^{-mu/kT}. \quad (3-30)$$

Therefore the average energy \bar{E} of an oscillator is

$$\bar{E} = \frac{\sum_{m=0}^{\infty} mun_0 e^{-mu/kT}}{\sum_{m=0}^{\infty} n_0 e^{-mu/kT}}. \quad (3-31)$$

Since m is an integer, Eq. (3-16) becomes

$$\bar{E} = \frac{0 + ue^{-u/kT} + 2ue^{-2u/kT} + 3ue^{-3u/kT} + \dots}{1 + e^{-u/kT} + e^{-2u/kT} + e^{-3u/kT} + \dots}. \quad (3-32)$$

Let $x = e^{-u/kT}$. Then Eq. (3-17) can be written

$$\bar{E} = ux \frac{1 + 2x + 3x^2 + \cdots}{1 + x + x^2 + \cdots} \quad (3-33)$$

The limits of these convergent series can be found by the usual methods (note that $x < 1$). The convergence limit of the series in the numerator is $1/(1-x)^2$. This can be checked by expanding $(1-x)^2$ according to the binomial theorem. The denominator is a simple geometric progression converging to $1/(1-x)$. Substituting these limits in Eq. (3-33), we have

$$\bar{E} = ux \frac{1/(1-x)^2}{1/(1-x)} = \frac{ux}{1-x} = \frac{u}{(1/x) - 1} \quad (3-34)$$

When x is replaced by its equivalent, the result is

$$\bar{E} = \frac{u}{e^{u/kT} - 1} \quad (3-35)$$

If we now multiply Eq. (3-35) by the number of modes of vibration in a unit volume of cavity space, from Eq. (3-25), we obtain the energy density in a wavelength range $d\lambda$,

$$\Psi_\lambda = \frac{8\pi}{\lambda^4} \frac{u}{e^{u/kT} - 1} d\lambda \quad (3-36)$$

Recall that in this derivation the energy of an oscillator has been assumed to be an integer, m , times some small energy, u . Classical physics says the energy may have any value. This is equivalent to saying u may be exceedingly small and, in the limit, approach zero. If we set $u = 0$, Eq. (3-35) is indeterminate, $0/0$. If we apply l'Hospital's rule, differentiating both numerator and denominator with respect to u before letting $u = 0$, we find that

$$\bar{E} = kT, \quad (3-37)$$

which is in complete agreement with Rayleigh's classical assumption of continuous energy. As we have seen, however, this assumption does not lead to the correct radiation law.

The relation given in Eq. (3-36) begins to look like Planck's empirical law (Eq. 3-27), if u is not zero. Indeed, the denominators of these two equations become identical (except for the minus one) if a value of u is chosen so that the powers of the exponential terms are the same. To obtain this value of u , we let

$$\frac{c_2}{\lambda T} = \frac{u}{kT}, \quad (3-38)$$

or

$$u = \frac{c_2 k}{\lambda} = \frac{c_2 k}{c} \nu. \quad (3-39)$$

In this last equation, c is the free-space velocity of light and ν is the frequency of the oscillator and therefore also the frequency of the radiation it emits. If we replace the constants $(c_2 k/c)$ by another constant h , we have

$$u = \frac{hc}{\lambda} = h\nu. \quad (3-40)$$

When the value of u from Eq. (3-40) is substituted in Eq. (3-36), we obtain Planck's law for the energy density of black-body or cavity radiation. This law is

$$\Psi_\lambda d\lambda = \frac{8\pi ch\lambda^{-5}}{e^{hc/\lambda kT} - 1} d\lambda. \quad (3-41)$$

This equation does agree with the experimental results. It is plotted in Fig. 3-7 (solid curve) for a temperature $T = 1646^\circ\text{K}$.

When we introduced the idea of discrete energy steps u , we did not indicate that u would be different for the different modes. However, this is what our analysis has shown to be the case. Going back to Fig. 3-9(b), we can now explain qualitatively how Planck avoids the ultraviolet catastrophe. For small wavelengths, high frequencies, the distance from $E = 0$ to the first discrete energy level u is so large that the probability for a mode to exist in that state of excitation becomes diminishingly small. All modes of very high frequency therefore have $E = 0$. This is also immediately evident from Eq. (3-35).

The new constant h is called the *Planck constant*. We have seen that it could be determined from Wien's constant c_2 but it can also be evaluated from the photoelectric effect discussed later in this chapter. Its value is $h = (6.62620 \pm 0.00005) \times 10^{-34} \text{ J}\cdot\text{s}$. (Note that the units are those of angular momentum.)

Thus Planck was led to his startling, nonclassical assumption that the energy states of an oscillator must be an *integral* multiple of the product of the constant h and the frequency ν of the electromagnetic radiation it emits. If E represents the smallest permissible energy change, Planck's famous quantum* equation is

$$E = h\nu. \quad (3-42)$$

Planck introduced the quantum concept in 1900, and it eventually led to the conclusion that radiation is not emitted in continuous amounts but in discrete bundles of energy each equal to $h\nu$. These bundles or packets of radiant energy are now called *quanta* or *photons*. This was the beginning of the atomic theory of radiation, which has grown to become the quantum theory. It is obvious, however, that quanta of radiation of different frequencies have different "sizes" (energies), and that they are atomic only in the sense that they are

* Quantum is the Latin word for *how much* or *how great*.

discrete. Planck thought at first that his *ad hoc** hypothesis applied only to the oscillators and, possibly, to the emitted radiation in their immediate neighborhood and that, at most, it was a slight modification of Maxwell's theory of radiation. However, we shall see that he initiated a series of events which have changed our whole concept of the interaction of electromagnetic radiation with matter.

3-11 PHOTOELECTRIC EFFECT

We now turn from thermal radiation to another portion of the electromagnetic spectrum and consider an effect which is due to radiation of higher frequency. We mentioned earlier that even before the discovery of the electron, Hallwachs observed that zinc irradiated with ultraviolet light lost negative charge. He proposed that somehow the radiation caused the zinc to eject negative charge. In 1899 Lenard showed that the radiation caused the metal to emit electrons.

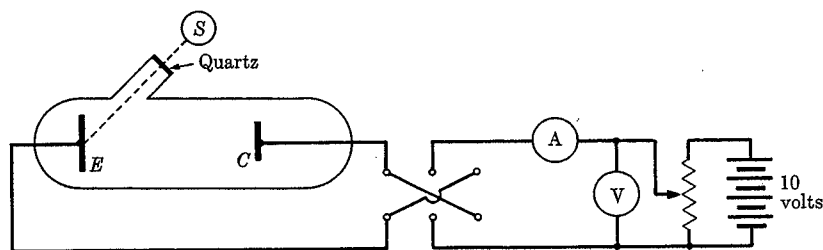


Fig. 3-10 Apparatus for investigating the photoelectric effect.

This phenomenon, called the photoelectric effect, can be studied in detail with the apparatus shown in Fig. 3-10. In this figure, S is a source of radiation of variable and known frequency ν and intensity I , E is an emitting electrode of the material being studied, and C is a collecting electrode. Both electrodes are contained in an evacuated glass envelope with a quartz window that permits the passage of ultraviolet and visible light. The electric circuit allows the electrodes to be maintained at different known potentials and permits the measurement of any current between the electrodes. We first make the collecting electrode positive with respect to the emitting electrode, so that any electrons ejected will be quickly swept away from the emitter. About 10 V is enough to do this but not enough to free electrons from the negative electrode by positive-ion bombardment as was the case in the early cathode-ray tubes. If the tube is dark, no electrons are emitted and the microammeter indicates no current. If ultraviolet light is allowed to fall on the emitting electrode, electrons

* *Ad hoc* means literally *to this*, and is used to describe a hypothesis which is applicable to but one (this) situation.

are liberated and the current is measured by the microammeter. It is found that the rate of electron emission is proportional to the light intensity. By holding the frequency ν of the light and the accelerating potential V constant, we can obtain data like that represented in Fig. 3-11.

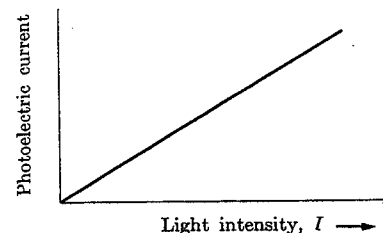


Fig. 3-11 Photoelectric current as a function of the intensity of the light. The frequency of the light and the accelerating potential are kept constant.

It is hardly surprising that if a little light liberates a few electrons, then more light liberates many. If we vary either the frequency of the light or the material irradiated, only the slope of the line changes.

We can now experiment by keeping the light intensity constant and varying the frequency. The graphs of these data are shown in Fig. 3-12, where A and B represent two different irradiated materials. The significant thing about these curves is that for every substance irradiated there is a limiting frequency below which no photoelectrons are produced. This frequency, called the *threshold frequency*, ν_0 , is a characteristic of the material irradiated. The wavelength of light corresponding to the threshold frequency is the *threshold wavelength*, λ_0 . No photoelectrons are emitted for wavelengths greater than this.

The existence of a threshold frequency is difficult to explain on the basis of the wave theory of light. If we think of light as consisting of a pulsating electromagnetic field, we can imagine that that field is sometimes directed so as to tend to eject electrons from a metallic surface. We might even feel it

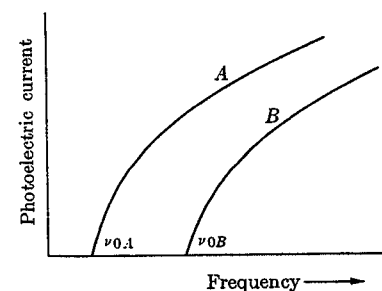


Fig. 3-12 Photoelectric current for two materials as a function of the frequency of the light. The intensity of the light and the accelerating potential are kept constant.

reasonable that certain frequencies of light would resonate with the electrons of the metal so that, for a particular metal, there might be preferred light frequencies which would cause emission more efficiently. The striking thing about these data is that for each material there is a frequency below which no photoelectrons are emitted and above which they are emitted. This effect is independent of the intensity of the light.

In 1905 Einstein proposed a daring but simple explanation. He centered attention on the energy aspect of the situation. Whereas Planck had proposed that radiation was composed of energy bundles only in the neighborhood of the emitter, Einstein proposed that these energy bundles *preserve their identity throughout their life*. Instead of spreading out like water waves, Einstein conceived that the emitted energy bundle stays together, and carries an amount of energy equal to $h\nu$. For Einstein, the significance of the light frequency was not so much an indication of the frequency of a pulsating electric field as it was a measure of the energy of a bundle of light called a *photon*. His interpretation of the data of Fig. 3-12 would be that a quantum of light below the threshold frequency just does not have enough energy to remove an electron from the metal, but light above that frequency does.

The threshold frequency is dependent on the nature of the material irradiated because there is for each material a certain minimum energy necessary to liberate an electron. The *photoelectric work function* or *threshold energy*, W_0 , of a material is the *minimum* energy required to free a photoelectron from that material.

In a third photoelectric experiment let us hold both the frequency and intensity of the light constant. The variable is the potential difference across the photoelectric cell. Starting with the collector at about 10 volts positive, we reduce this potential to zero and then run it negative until the photocurrent stops entirely. Curve I_1 of Fig. 3-13 shows the type of curve we might expect for this particular substance. This curve requires careful interpretation.

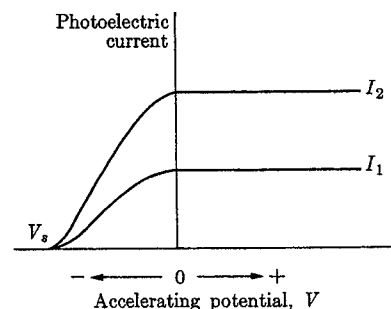


Fig. 3-13 Photoelectric current as a function of the accelerating potential for light of different intensities having a two-to-one ratio. The frequency of the light is constant.

When the potential difference across the tube is about 10 V or more, *all* the emitted electrons travel across the tube. This stream of charges is called the *saturation current*, and it is obvious that an increase in the potential of the collector cannot cause an increase in current. As the accelerating potential is reduced from positive values through zero to negative values, the tube current reduces because of the applied retarding potential. Eventually this potential is large enough to stop the current completely.

The *stopping potential* V_s is the value of the retarding potential difference that is just sufficient to halt the *most energetic* photoelectron emitted. Therefore the product of the stopping potential and the electronic charge, $V_s e$, is equal to the maximum kinetic energy that an emitted electron can have. Since this stopping potential has a definite value, it indicates that the emitted electrons have a definite upper limit to their kinetic energy. Doubling the intensity of the light doubles the *current* at each potential, as in I_2 of Fig. 3-11, but the stopping potential is *independent* of the intensity.

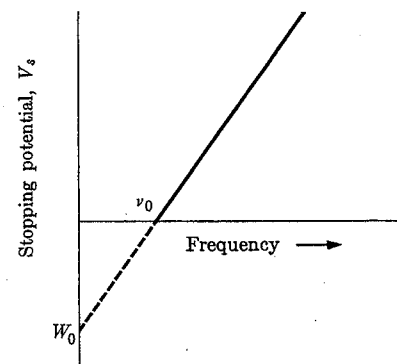


Fig. 3-14 Stopping potential as a function of the frequency of the light. Results are independent of intensity.

If, however, the experiment is repeated with a series of different light frequencies, it is found that the stopping potential increases linearly with the frequency. This is best shown by plotting the stopping potential against the frequency, as shown in Fig. 3-14. Below the threshold frequency no electrons are emitted and the stopping potential is of course zero; however, as the frequency is increased above the threshold, the stopping potential increases linearly with the frequency.

To see how fully the data of Fig. 3-14 confirm the Einstein photon interpretation of the photoelectric effect, we now interpret the graph of Fig. 3-14 as he would have. For light frequency between zero and the threshold frequency there are no photoelectrons produced, since the incident photons have

less energy than the work function of the material. For light above the threshold frequency, photoelectrons are emitted. The energy of these emitted electrons may vary greatly. According to the Einstein view, however, there must be an upper limit to the energy of the emitted photoelectrons. No photoelectrons can have energy in excess of the energy of the incoming photon less the minimum energy to free an electron, the work function. Since the photon energy is proportional to frequency and since the stopping potential is a measure of the maximum kinetic energy of the emitted photoelectrons, the graph of stopping potential against frequency should be a straight line. This is precisely what Fig. 3-14 shows. The quantitative check of the Einstein interpretation is that the slope of the straight line provides a method of determining the way in which photon energy depends on photon frequency, which is the Planck constant.

A final and decisive experiment consists of making the irradiating light extremely weak. In this case, the number of photoelectrons is very small and special techniques are required to detect them. The significant result of this experiment is that dim light causes emission of photoelectrons which, however few, are emitted instantaneously and with the same maximum kinetic energy as for bright light of the same frequency.

According to the wave theory of light, pulsating electromagnetic fields spread out from their source. Dim light corresponds to waves of small amplitude and small energy. If dim light spreads over a surface, conservation of energy requires that either no photoelectrons should be emitted or the electrons must store energy over long periods of time before gathering enough energy to become free of the metal. The fact that high-energy photoelectrons appear immediately can be explained only by assuming that the light energy falls on the surface in concentrated bundles. According to Einstein, the dim light consists of a few photons each having energy depending only on the light frequency. This energy is not spread over the surface uniformly as required by the wave theory. A photon that is absorbed gives all its energy to one electron, and that electron will be emitted violently even though the number of such events is small.

If a man dives into a swimming pool, his energy is partly converted into waves which agitate other swimmers in the pool. If it were observed that when a man dives into a pool another swimmer is suddenly ejected from the pool onto a diving board, we would be forced to conclude that the energy provided by the diver did not spread out in an expanding wavefront, but was somehow transferred in concentrated form to the ejected swimmer. A swimming party held in such a superquantum pool would be a very odd affair compared with one in a classical pool.

To summarize Einstein's interpretation of the photoelectric effect, we equate the energy of an incident photon of frequency ν to the sum of the work function of the emitter ($W_0 = h\nu_0$) and the maximum kinetic energy that an

ejected photoelectron can acquire. We then have

$$h\nu = h\nu_0 + \frac{1}{2}m_e v_{\max}^2, \quad \text{or} \quad \frac{1}{2}m_e v_{\max}^2 = h\nu - h\nu_0,$$

or

$$V_s e = h\nu - W_0. \quad (3-43)$$

This is a linear equation. It is the equation of the graph in Fig. 3-14. It is evident that the slope of the curve V_s plotted as a function of ν is equal to h/e , that ν_0 is the ν -axis intercept, and that W_0/e is the intercept of the extrapolated curve on the V_s -axis. Einstein's photoelectric equation was first verified with precision in 1916, eleven years after it was proposed, by Millikan, who made careful measurements of the photoemission from many different substances.

3-12 SUMMARY OF THE ATOMIC VIEW OF RADIATION

We introduced this chapter by outlining the disagreement between Newton and Huygens over the nature of light. We described how Maxwell strengthened Huygens' wave theory when he showed that electromagnetic waves were a consequence of the laws of electricity and magnetism. We reported that Hertz demonstrated that electric circuits could be made to produce the electromagnetic waves Maxwell predicted. But we also mentioned that Hertz observed that he could produce sparks more easily when his spark gap was illuminated. Thus Hertz's work, which supported Maxwell's theory, also contained the first observation of the photoelectric effect. Although the wave theory of light accounts beautifully for many optical phenomena, it fails to account for either the black-body radiation or the photoelectric effect, where light appears to possess marked particle aspects. It is hardly satisfactory to regard light as a wave motion part of the time and a particle phenomenon at other times. We shall return to the question of the resolution of this conflict of viewpoint in Chapter 5. At this point it is clear, however, that the resolution of this paradox can never eliminate the idea that light is emitted and absorbed in bundles of energy called photons, and that now radiation must join matter and electricity in having a basically atomic character. *The fact that radiant energy is quantized is a radical departure from classical physics and will require us to re-examine the whole energy concept from the quantum point of view.* Establishing this fact has been the main business of this chapter. Before closing the chapter, however, we shall consider some related topics.

3-13 THE ELECTRON VOLT; PHOTON ENERGIES

In the Einstein equation, we measured the maximum kinetic energy of the emitted electrons by noting the potential energy difference (eV_s), which was

equivalent to the electron kinetic energy. This method of determining and expressing electron energies is a particularly convenient one, and it suggests a new unit of energy. This new unit of energy is called the *electron volt*, eV, which is defined as the amount of energy equal to the change in kinetic energy of one electronic charge when it moves through a potential difference of one volt. Since the electron volt is an energy unit, it is in the same category as the joule, the foot-pound, the British thermal unit, and the kilowatt-hour.

Energies in joules can be converted to electron volts by dividing by $e_c = 1.60 \times 10^{-19}$. In this case e_c is *not* a charge but a *conversion factor* having the units of joules per electron volt. The Einstein equation, Eq. (3-43), is valid in any consistent system of units. If we choose MKSA units and divide Eq. (3-43) by the factor e_c , we obtain the same relation in electron volts:

$$E_{k(\max)} \text{ (numerically equal to } V_s) = \frac{h\nu}{e_c} - \frac{W_0}{e_c}. \quad (3-44)$$

In words, this equation states that the maximum kinetic energy of a photoelectron in electron volts equals the energy of the photon in electron volts minus the work function in electron volts.

When the electron volt is too small a unit, it is convenient to use $10^3 \text{ eV} = 1 \text{ keV}$ (kilo-electron-volt), and $10^6 \text{ eV} = 1 \text{ MeV}$ (million-electron-volt).

It is also useful to express photon energies in electron volts. In terms of photon frequency,

$$E = \frac{h\nu}{e_c} = \frac{6.63 \times 10^{-34}}{1.60 \times 10^{-19}} \nu \text{ eV} = 4.14 \times 10^{-15} \nu \text{ eV}. \quad (3-45)$$

Or, since $\nu = c/\lambda$, we get

$$\begin{aligned} E &= \frac{4.14 \times 10^{-15} \times 3 \times 10^8}{\lambda} \text{ eV} \\ &= \frac{1.24 \times 10^{-6}}{\lambda} \text{ eV}, \end{aligned} \quad (3-46)$$

with λ in meters. If the wavelength is expressed in angstroms instead of meters, we have

$$E = \frac{1.24 \times 10^4}{\lambda} \text{ eV}. \quad (3-47)$$

We shall use Eq. (3.47) frequently.

Example. Light having a wavelength of 5000 \AA falls on a material having a photoelectric work function of 1.90 eV . Find (a) the energy of the photon in eV, (b) the kinetic energy of the most energetic photoelectron in eV and in joules, and (c) the stopping potential.

Solution.

a) From Eq. (3-47),

$$E = \frac{1.24 \times 10^4}{5000} = 2.47 \text{ eV}.$$

b) The law of conservation of energy gives

$$\text{maximum kinetic energy} = \text{photon energy} - \text{work function}$$

or

$$E_k = 2.47 \text{ eV} - 1.90 \text{ eV} = 0.57 \text{ eV}.$$

Also

$$E_k = 0.57 \times 1.60 \times 10^{-19} = 9.11 \times 10^{-20} \text{ J}.$$

$$(c) \quad V_s = \frac{0.57 \text{ eV}}{1 \text{ electronic charge}} = 0.57 \text{ V}.$$

3-14 THERMIONIC EMISSION

The subjects discussed in this and the next section are, strictly speaking, not parts of "The Atomic View of Radiation," but their relations to the topics discussed earlier in this Chapter are such that, pedagogically as well as historically, they belong here.

We have already considered two ways in which electrons can be released from a metal. In Chapter 2 we discussed the discharge of electricity through gases. The electrons that participate in cold-cathode discharges are obtained from the cathode while it is bombarded by the positive ions produced in the residual gas in the tube. In this chapter we have considered another emission process, called photoelectric emission. There is still another kind of electron emission, which we shall now discuss briefly.

If a metal is heated, the thermal agitation of the matter may give electrons enough energy to exceed the work function of the material. Thus the space around a heated metal is found to contain many electrons. A study of this effect shows that the *thermionic work function* is very nearly the same as the photoelectric work function—a most satisfying result.

Since a fine wire can be heated easily by passing an electric current through it, thermionic emission is one of the most convenient electron sources. Most radio-type vacuum tubes use a heated cathode as their electron source. Thermal emission of negative charges from a hot wire in a vacuum was first observed by Edison in 1883 when he was making incandescent lamps, and such thermal emission is called the *Edison effect*. In 1899, J. J. Thomson, showed that the thermions in this effect are electrons.

3-15 SPECIFIC HEAT OF SOLIDS

In Section 1-4, we mentioned an experimental law discovered by Dulong and Petit in 1819 stating that the product of the atomic mass and specific heat is

the same for all elementary (solid) substances. It can be restated to read: "The specific heat per mole is the same for all solid substances." This law was based on early measurements of the specific heat for a series of substances. All these measurements were taken at room temperature. The value found for the specific heat per mole was approximately $6 \text{ cal} \cdot \text{mole}^{-1} \text{ } ^\circ\text{C}$.

As discussed in Section 1-7, the temperature of a gas is a direct measure of its translation kinetic energy. Similarly, the temperature of a solid is a measure of the kinetic energy of the atoms as they perform vibrations about the equilibrium positions in the lattice structure. At the interphase between the solid and the gas there will exist an equilibrium of no net energy flow if the temperature of the solid is the same as the temperature of the gas. Since the gas molecules and the atoms in the solid are constantly colliding with each other, they have, in equilibrium, the same average kinetic energy. This means that each atom in the solid has an average kinetic energy of $\frac{3}{2}kT$. Since these atoms are vibrating as harmonic oscillators, they will also on the average have potential energy. It is well known from mechanics that, in the harmonic oscillator, the average potential energy equals the average kinetic energy. Therefore the total energy per atom is $3kT$. The total energy content per mole is therefore

$$E = 3kN_A T = 3RT, \quad (3-48)$$

with $R = kN_A$ being the gas constant. The specific heat per mole is therefore

$$c_v = dE/dT = 3R = 5.94 \text{ cal} \cdot \text{mole}^{-1} \text{ } ^\circ\text{K}^{-1}, \quad (3-49)$$

in agreement with Dulong and Petit's law.

In this simple derivation we have assumed that the substances undergo no change in phase, that is, change of the crystalline structure of the solid, during heating. We have also disregarded any effect resulting from changes of energy of the so-called "free" electrons in metals. As further discussed in Chapter 11, only a very small fraction of these free electrons increase their energy as the solid is heated. Therefore the effect on the specific heat of this energy increase is negligibly small.

It was very soon shown that Dulong and Petit's law for some substances failed quite badly at room temperature and that for all substances the specific heat decreases with the absolute temperature. Figure 3-15 shows as examples the specific heats of diamond, silicon, aluminum, and lead as functions of the absolute temperature. As the temperature increases, the specific heat for all these substances approaches approximately the value $3R$ predicted above. However, our simple derivation fails to account for the decrease towards absolute zero. Einstein in 1907* was able to explain the basic features of the curves shown in Fig. 3-15. He assumed that the energy of oscillations of the vibrating atoms is quantized in exactly the same way as the modes of electro-

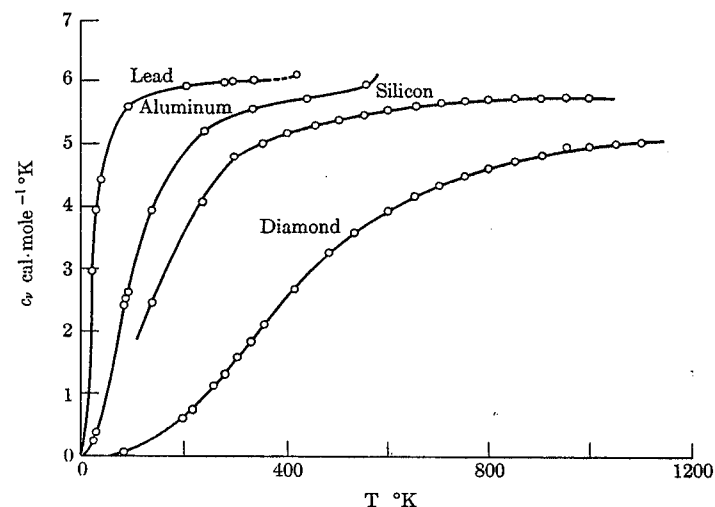


Fig. 3-15 Variation of specific heat at constant volume with temperature. Reproduced by permission from Richtmyer, Kennard, and Lauritsen, *Introduction to Modern Physics*, New York: McGraw-Hill © 1955, p. 410.

magnetic oscillation in an isothermal enclosure (Section 3-10). Accordingly, the average energy per oscillator is not $3kT$ but

$$\bar{E}_0 = \frac{3h\nu}{e^{h\nu/kT} - 1} \quad (3-50)$$

(compare Eq. 3-35). The frequency ν is now the vibrational frequency of the atom in the lattice of the crystal. We find the total energy E per mole by multiplying \bar{E}_0 by Avogadro's constant N_A . The specific heat per mole is then

$$c_v = \frac{dE}{dT} = 3R \frac{e^{h\nu/kT}}{(e^{h\nu/kT} - 1)^2} \left(\frac{h\nu}{kT} \right)^2. \quad (3-51)$$

The frequency of vibration of an atom in a solid can be estimated in various ways. For instance, by measuring the compressibility of the solid, one can estimate the "spring constant" for the restoring forces; and, of course, the mass of the atom is known. By using such techniques, one was able to show that Einstein's theory was in qualitative agreement with experimentally observed specific heats.

The assumption of one single vibrational frequency is an oversimplification. Debye* improved Einstein's formula by assuming that the vibrational frequencies had a broad spectrum up to a maximum value and that there are two

* A. Einstein, *Ann. Physik* 22 (1907), p. 180.

* P. Debye, *Ann. Physik* 39 (1912), p. 789.

types of vibrations, one transverse and one longitudinal. However, of central importance also in Debye's derivation is the average energy per degree of freedom as given by Planck's formula. Thus Einstein and Debye showed that the concept of quantization of energy is not limited to electromagnetic radiation in an isothermal cavity, but also to mechanical harmonic oscillators. In the next chapter, we shall see how Niels Bohr found that the energies of electrons in atoms are quantized and also that their angular momenta are quantized. It fell on Erwin Schrödinger (Chapter 6) with some help of others to tie all these loose ends together in a neat theory that we call *wave mechanics*.

PROBLEMS

- 3-1 The displacement x at time t of mass m which is moving with simple harmonic motion of amplitude A and frequency ν is given by $x = A \sin 2\pi\nu t$. a) Show that its kinetic energy T is $2\pi^2\nu^2 A^2 m \sin^2 2\pi\nu t$. b) Show that the time average of T over a whole cycle and the time average of V over a whole cycle are each equal to one-half the total energy of the oscillator, $2\pi^2\nu^2 A^2 m$.
- 3-2 Show that Planck's radiation law, Eq. (3-41), reduces to Wien's law for short wavelengths and to the Rayleigh-Jeans' law for long ones. (*Hint*: Express the exponential term as a series to obtain the second of these laws.)
- 3-3 The cavity of a black-body radiator is in the shape of a cube measuring 2 cm on a side and the black body is at a temperature of 1500°K. a) Find the number of modes of vibration per unit volume in the cavity in the wavelength band between 4995 Å and 5005 Å. b) Calculate the radiant energy in the whole cavity in this wavelength band of 10 Å (1) by assigning an energy of kT to each mode of vibration and (2) from Planck's radiation law.
- 3-4 Show that the energy density of black-body radiation expressed in terms of frequency is

$$\psi_\nu = \frac{8\pi h\nu^3}{c^3(e^{h\nu/kT} - 1)} d\nu.$$

- 3-5 Show that the total energy density in black-body radiation over the whole range of frequencies from 0 to ∞ is identical in form to the Stefan-Boltzmann law for total radiation. A useful definite integral is

$$\int_0^\infty \frac{x^3 dx}{e^x - 1} = \frac{\pi^4}{15}.$$

- 3-6 a) Show that the maximum energy density in the spectrum of black-body radiation occurs at a wavelength λ_m which can be found from the equation $(1 - x/5)e^x = 1$, where $x \equiv ch/\lambda_m kT$. b) Find the roots of this equation, and then show that $\lambda_m T = 2.90 \times 10^{-3}$ m °K.
- 3-7 At the surface of the earth a 1-cm² area oriented at right angles to the sun's rays receives about 0.13 J of radiant energy each second. Assume that the sun is a black-body radiator. What is the surface temperature of the sun? (The radius of the sun is about 7×10^8 m and the earth is about 1.49×10^8 km from the sun.)

- 3-8 A tungsten sphere 0.5 cm in radius is suspended within a large evacuated enclosure whose walls are at 300°K. Tungsten is not a black body but has an average emissive power that is 0.35 that of a black body. What power input is required to maintain the sphere at a temperature of 3000°K if heat conduction along the supports is neglected?
- 3-9 Find the percent change in the total energy radiated per unit time by a black body if the absolute temperature of the black body is increased by a) 100 percent, b) 10 percent, c) 1 percent, and d) 0.1 percent.
- 3-10 At what wavelength does the maximum intensity of the radiation from a black body occur at a temperature of 300°K? 1000°K? 6000°K?
- 3-11 If 5 percent of the energy supplied to an incandescent light bulb is radiated as visible light, how many visible quanta are emitted per second by a 100-watt bulb? Assume the wavelength of all the visible light to be 5600 Å.
- 3-12 In order that an object be visible to the naked eye, the intensity of light entering the eye from the object must be at least 1.5×10^{-11} J · m⁻² · s⁻¹. What is the minimum rate at which photons must enter the eye so that an object is visible, given that the diameter of the pupil is 0.7 cm? Assume a wavelength of 5600 Å.
- 3-13 What is the energy in eV of a photon having a wavelength of 912 Å?
- 3-14 Show that Planck's constant h has the same physical units as angular momentum.
- 3-15 A mass of 10 g hangs from a spring with a force constant of 25 N m⁻¹. Assume that this oscillator is quantized just as the radiation oscillators are. a) What is the minimum energy that can be supplied to the mass? b) If the mass at rest absorbs the minimum energy of part a), what is the resulting amplitude? c) How many quanta must the mass absorb in order to have an amplitude of 10 cm?
- 3-16 Particles of a certain system can have energies of E , $2E$, or $3E$, where $E = 0.025$ eV. a) What are the ratios of the number of particles in each of the upper states to the number of particles in the lowest state when the system is in equilibrium at 290°K? b) What is the average energy of a particle in the equilibrium distribution of these states?
- 3-17 In a problem in Chapter 1, it was found that a thermal neutron has a velocity of 2200 m s⁻¹. a) What is a thermal neutron's kinetic energy in eV? b) What is the increase in kinetic energy in eV of each water molecule in a stream that goes down a 450-ft (137.1 m) waterfall?
- 3-18 The fissioning of a ²³⁵U atom yields 200 MeV of energy. How many such atoms must fission to provide an amount of energy equal to that required to lift a mosquito one inch? The mass of an average mosquito is 0.90 mg.
- 3-19 The visible light from a 40-watt incandescent bulb is incident normally on a potassium surface 50 cm from the bulb. a) How long will it take a potassium atom to absorb 2.0 eV of energy which is its photoelectric work function? Consider the bulb a point source that radiates 7.5 percent of the input power as visible light. Assume that the absorbing area of the potassium atom is equivalent to a circular disk having a diameter of 5.0 Å. b) How long would it take the potassium atom to absorb 2.0 eV of energy if it is illuminated by full moonlight? The illumination at 50 cm from a 40-watt bulb is about 740 times greater than full moonlight.

The Atomic Models of Rutherford and Bohr

3-20 The light-sensitive compound on most photographic films is silver bromide, AgBr. We shall assume that a film is exposed when the light energy absorbed dissociates this molecule into its atoms. (The actual process is more complex, but the quantitative result does not differ greatly.) The energy or heat of dissociation of AgBr is $23.9 \text{ kcal} \cdot \text{mole}^{-1}$. Find a) the energy in eV, b) the wavelength, and c) the frequency of the photon that is just able to dissociate a molecule of silver bromide. d) What is the energy in eV of a quantum of radiation having a frequency of 100 MHz? e) Explain the fact that light from a firefly can expose a photographic film, whereas the radiation from a television station transmitting 50,000 watts at 100 MHz cannot. f) Will photographic films stored in a light-tight container be ruined (exposed) by radio waves constantly passing through them? Explain.

3-21 When a certain photoelectric surface is illuminated with light of different wavelengths, the following stopping potentials are observed:

$\lambda, \text{\AA}$	3660	4050	4360	4920	5460	5790
V_s, V	1.48	1.15	0.93	0.62	0.36	0.24

Plot the stopping potential as ordinate against the frequency of the light as abscissa. Determine a) the threshold frequency, b) the threshold wavelength, c) the photoelectric work function of the material, and d) the value of the Planck constant h (the value of e being known).

3-22 The photoelectric work function of potassium is 2.0 eV. If light having a wavelength of 3600\AA falls on potassium, find a) the stopping potential, b) the kinetic energy in eV of the most energetic electrons ejected, and c) the velocities of these electrons.

3-23 What will be the change in the stopping potential for photoelectrons emitted from a surface if the wavelength of the incident light is reduced from 4000\AA to 3980\AA ? (Assume that the decrease in wavelength is so small that it may be considered a differential.)

3-24 The threshold wavelength for photoelectric emission from a certain material is 6525\AA . Find the stopping potential when the material is irradiated with a) light having a wavelength of 4000\AA , and b) with light having twice the frequency and three times the intensity of that in the previous part. c) If a material having double the work function were used, what would be the answers to parts a) and b)?

3-25 Light of wavelength 4000\AA liberates photoelectrons from a certain metal. The photoelectrons now enter a uniform magnetic field having an induction of 10^{-4} T . The electrons move normal to the field lines so that they travel circular paths. The largest circular path has a radius of 5.14 cm . Find the work function for the metal.

3-26 A surface is irradiated with monochromatic light of variable wavelength. Above a wavelength of 5000\AA , no photoelectrons are emitted from the surface. With an unknown wavelength a stopping potential of 3V is necessary to eliminate the photoelectric current. What is the unknown wavelength?

4-1 INTRODUCTION

We have traced how matter, electricity, and radiation came to be regarded as atomic in character. We have established the existence of some elementary particles that are more fundamental than the chemical elements. Electrons, for example, are common to all elements and are a common building block of all matter. Our discussion of positive rays and mass spectroscopy showed that matter also has positive constituents which are much more massive than electrons. Thomson, who made the first quantitative measurements on electrons and positive rays, assumed that a normal chemical atom consists of a mixture of constituents. This mixture came to be called the "plum-pudding" atomic model: The atom was regarded as a heavy positive sphere of charge seasoned with enough electron plums to make it electrically neutral.

4-2 PROBING THE ATOM WITH ALPHA PARTICLES

A very different atomic model was indicated by experiments performed by Rutherford and his associates in 1911.

We shall discuss radioactivity at some length in Chapter 12, but in order to be able to discuss the Rutherford experiments a few observations need to be made now. Certain atoms are unstable and fly apart of their own accord. The nature of these disintegrations depends on the element that is disintegrating, but in every case the fragments ejected consist either of electrons, here called beta rays, or of doubly ionized helium atoms, called alpha particles. These disintegration fragments usually are ejected with high energies from a radioactive substance and are often accompanied by very short-wavelength photon radiation called gamma rays. Radium, for example, is an excellent source of high-energy alpha particles. These alpha particles can travel through a few centimeters of air before they are stopped, and in a vacuum they travel long

distances without losing energy. When they strike certain materials, they cause visible fluorescent light flashes.*

Rutherford studied how these alpha particles from radium were absorbed by matter. He found they were absorbed by sheets of metal a few hundredths of a millimeter thick, but that they could readily pass through gold foil several ten-thousandths of a millimeter thick. Rutherford's apparatus is shown schematically in Fig. 4-1. Radium was placed in a cavity at the end of a narrow tunnel in a lead block. Alpha particles were emitted in random directions by this source and the lead absorbed all except those emitted along the axis of the tunnel. In this way Rutherford obtained a collimated beam of alpha particles which streamed toward the gold foil. Particles deflected by an angle θ by passage through the foil produced flashes on a ZnS fluorescent screen, and these flashes were observed in a low-power microscope.

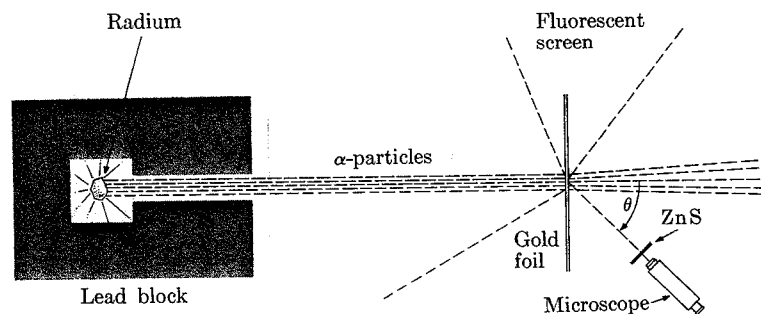


Fig. 4-1 Schematic diagram of Rutherford's alpha-particle scattering apparatus.

Many of the alpha particles did go straight through the foil or were deflected only by very small amounts. Amazingly, however, some alpha particles were deflected through very large angles. A few even returned to the side of the gold foil from which they came. Rutherford's astonishment at this is evident in his comment, "It was quite the most incredible event that has ever happened to me in my life. It was almost as incredible as if you fired a 15-inch shell at a piece of tissue paper and it came back and hit you." This observed scattering through large angles was contrary to predictions based on

* Radiolight watch dials are painted with a paste containing fluorescent material and a trace of radium. Under a microscope the glow of the dial can be seen to be a multitude of flashes, called scintillations, which remind one of the twinkling of the stars on a summer night. The effect may be seen through a 4-power magnifier, but it is better to use two or three times this magnification. The light is less likely to appear continuous if there is very little radioactive material on the dial. Observations must be made in a completely darkened room and it may be necessary to wait about five minutes for the eyes to become dark-adapted. This time delay will also permit any phosphorescence to fade and eventually die out.

the Thomson model of the atom. Let us examine these predictions in some detail.

Assume that an alpha particle of charge ze (with $z = 2$) collides with a Thomson atom of radius R . Can it be turned around in its path if the forces acting are only electrostatic forces? Before it starts on its way back, it must be momentarily at rest, and this means that the kinetic energy has been converted into potential energy. (Since the alpha particle is much lighter than the atom it is colliding with, we neglect the kinetic energy resulting from center-of-mass motion.) The potential energy for a particle of charge ze at the surface of a uniform-charge cloud of radius R and charge Ze is $V_c = zZe^2/4\pi\epsilon_0 R$. At the center of the charge cloud the potential energy is

$$V_c = \frac{3zZe^2}{8\pi\epsilon_0 R} \quad (4-1)$$

Inserting $z = 2$, $Z = 80$ (for example), $R \approx 1\text{Å} = 10^{-10}\text{ m}$, and the known values for e and ϵ_0 , we get after converting to electron volts $V_c = 3456\text{ eV}$. We have completely neglected the effect of the electrons, which, of course, neutralize the positive charge and therefore substantially reduce its effect. Indeed, only local fluctuations of charge within the atom can produce the forces we are looking for. Since the kinetic energy of the alpha particles used in the experiments by Rutherford and his associates was about 5 MeV, it is clear that a single collision with a Thomson atom could not result in anything but a very small angle of deflection. A collision with an electron cannot produce much deflection either, because of the fact that the electron is 7000 times lighter than the alpha particle. What about multiple collisions?

A simple but adequate theory of multiple collisions predicts that the number of particles deflected into a small solid angle centered about an angle of deflection θ should be

$$N(\theta) = N(0) \cdot e^{-\theta^2/2\sigma^2} \quad (4-2)$$

This is a Gaussian distribution, or standard distribution with σ being the standard deviation determining the width of the curve. Two of Rutherford's associates, Geiger and Marsden, measured the angular distribution of alpha particles scattered from a $0.4\text{ }\mu$ thick gold foil. They found that about 1 in 20,000 was scattered through an angle of more than 90 degrees. Geiger later determined the probable angle of deflection as $\theta_p = 0.87$ degree. The probable angle θ_p , defined as the angle which has a 50 percent likelihood of being exceeded, relates to the standard deviation as $\theta_p = 0.6745\sigma$. This gives $\sigma = 1.29^\circ$ for the experiment described above.* By inserting $\theta = 90^\circ$ and

* It is amusing to note that Rutherford in his very famous paper on scattering of alpha particles by matter refers to the probable angle as "the *most* probable angle of deflexion." The most probable angle, that is, the maximum in the standard distribution is clearly $\theta = 0$. Thus even great scientists err, and sometimes worse than this! The reference is E. Rutherford, *Phil. Mag.* **21** (1911), p. 669.

$\sigma = 1.29^\circ$, we find from Eq. (4-2), $N(90) = N(0) \times 10^{-1060}$. This is such an incredibly small number that it clearly is not worth the effort to work out the integrals to determine the fraction of the beam of particles deflected by more than 90 degrees.

4-3 RUTHERFORD'S NUCLEAR ATOM

Rutherford concluded that the large deflections must come about by *single* encounters between alpha particles and atoms and that therefore the atoms must be seats of much more intense electric fields than those that would seem to be consistent with the Thomson model. He assumed that the positive massive part of the atom was concentrated in a very small volume at the center of the atom. This core, now called the *nucleus*, is surrounded by a cloud of electrons, which makes the entire atom electrically neutral. Because the atom is mostly empty space, many of the alpha particles go through the foil with practically no deviation. But an alpha particle that passes close to a nucleus experiences a very large force exerted by the massive positive core and is deflected through a large angle in a single encounter. From Eq. (4-1) and the example following it, it is clear that the radius of the nucleus must be more than 1000 times smaller than the radius of the atom if this is to stop an alpha particle and turn it around in its path. Collisions with electrons result in but very small deflections and can therefore be neglected.

We shall study the mechanics of a single encounter between an alpha particle and a nucleus, with the objective of finding a formula to replace Eq. (4-2) for the angular distribution of alpha particles scattered by a foil.

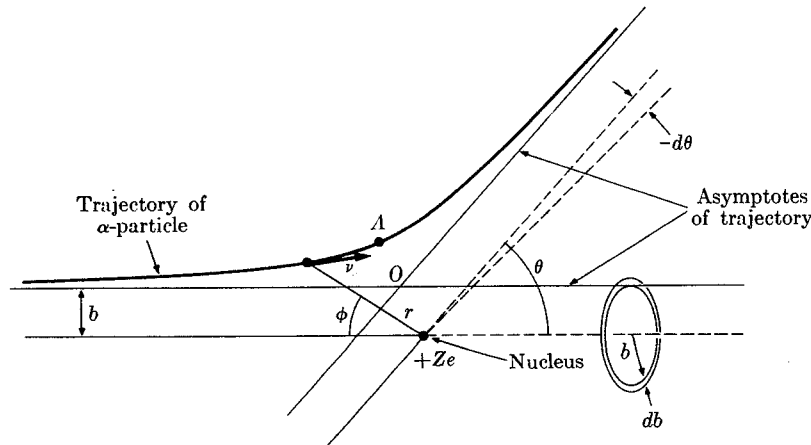


Fig. 4-2 Scattering of an alpha particle by the Rutherford nuclear atom.

Figure 4-2 shows the trajectory of an alpha particle approaching the nucleus with an impact parameter b . This is the distance between the nucleus and the straight-line path the alpha particle would have taken in the absence of an interaction. We use a polar coordinate system (r, ϕ) , as indicated in Fig. 4-2, and write the law of conservation of energy,

$$\frac{1}{2} m \left(\frac{dr}{dt} \right)^2 + \frac{1}{2} m r^2 \left(\frac{d\phi}{dt} \right)^2 + \frac{zZe^2}{4\pi\epsilon_0 r} = \frac{1}{2} m v_0^2, \quad (4-3)$$

where v_0 is the initial asymptotic velocity of the alpha particle. We have assumed that the nucleus is so much heavier than the alpha particle that we can neglect recoil.

The law of conservation of angular momentum yields

$$m r^2 \frac{d\phi}{dt} = m v_0 b$$

or

$$\frac{d\phi}{dt} = \frac{v_0 b}{r^2}. \quad (4-4)$$

We now introduce for convenience a parameter $2q$ which is equal to the distance of closest approach in a *head-on* collision:

$$2q = \frac{zZe^2}{2\pi\epsilon_0 m v_0^2}. \quad (4-5)$$

Combining Eqs. (4-3), (4-4), and (4-5), we get

$$\frac{dr}{dt} = \mp v_0 \left(1 - \frac{2q}{r} - \frac{b^2}{r^2} \right)^{1/2}. \quad (4-6)$$

The double sign arises from the square root. The radial velocity dr/dt is clearly first negative, then changes sign to positive at the position of minimum distance to the nucleus (Fig. 4-2). By again combining Eq. (4-6) with Eq. (4-4), we obtain

$$\frac{d\phi}{dr} = \mp \frac{b}{r^2} \left(1 - \frac{2q}{r} - \frac{b^2}{r^2} \right)^{-1/2}. \quad (4-7)$$

This is a differential equation describing the orbit in polar coordinates (r, ϕ) . Using a table of integrals, we find for the first part of the orbit from $r = \infty$ to point A in Fig. 4-2

$$\phi = \text{Arc cos} \left[\frac{b}{(b^2 + q^2)^{1/2}} \left(1 - \frac{2q}{r} - \frac{b^2}{r^2} \right)^{1/2} \right] - \text{Arc cos} \frac{b}{(b^2 + q^2)^{1/2}}. \quad (4-8)$$

We have integrated from ∞ to r and used the minus sign in Eq. (4-7). At the point of minimum r , we have $dr/dt = 0$, which inserted into Eq. (4-6) gives

$$1 - \frac{2q}{r} - \frac{b^2}{r^2} = 0$$

at point A . The angle ϕ corresponding to this point is, by Eq. (4-8),

$$\phi_A = \frac{\pi}{2} - \text{Arc cos } \frac{b}{(b^2 + q^2)^{1/2}}. \quad (4-9)$$

The orbit is symmetric about point A , since $d\phi/dr$ numerically depends upon r only and not upon ϕ as well (Eq. 4-7). The radius vector r therefore sweeps through a total angle $2\phi_A$. From Fig. 4-2, we see that the total angle of deflection is

$$\theta = \pi - 2\phi_A = 2 \text{ Arc cos } \frac{b}{(b^2 + q^2)^{1/2}}. \quad (4-10)$$

From this we find

$$\cos \frac{\theta}{2} = \frac{b}{(b^2 + q^2)^{1/2}}, \quad (4-11)$$

and easily

$$\sin \frac{\theta}{2} = \frac{q}{(b^2 + q^2)^{1/2}}. \quad (4-12)$$

Combining Eqs. (4-11) and (4-12), we get

$$b = q \cot \frac{\theta}{2}. \quad (4-13)$$

This, then, is a simple relationship between the impact parameter b and the total angle of deflection θ .

Our objective was to find a formula for the angular distribution of particles scattered by a foil representing a large number of scattering centers (nuclei). We can best do that by calculating the collision cross section (Section 1-10) for the process. First we shall modify this concept slightly. In Section 1-10, the cross section for a collision process represented a target area. A hit in this area resulted in deflection of the "bullet" particle. Nothing was said about the direction of the scattered particle after the collision. Figure 4-2 indicates a ring, displaced to the right for clarity, representing a target area for all alpha particles with impact parameters between b and $b + db$. This area is

$$d\sigma = 2\pi b db. \quad (4-14)$$

All particles aimed at that area will have a scattering angle between θ and $\theta + d\theta$, where θ is given by Eq. (4-13), and $d\theta$ by the differential of same:

$$db = -\frac{q}{2 \sin^2 \theta/2} d\theta. \quad (4-15)$$

The angles θ and $\theta + d\theta$ define two cones with the horizontal line through the nucleus as their axis (Fig. 4-2). The solid angle between the two cones is $d\Omega = 2\pi \sin \theta d\theta$, and this is therefore the solid angle into which particles aimed at the target area $d\sigma$ will be scattered. By substitution we now get from Eq. (4-14), neglecting the minus sign,

$$d\sigma = \frac{\pi q^2 \cos \phi/2 d\theta}{\sin^3 \theta/2} = \frac{q^2 2\pi \sin \theta d\theta}{4 \sin^4 \theta/2} = \frac{q^2 d\Omega}{4 \sin^4 \theta/2}. \quad (4-16)$$

Finally, we insert q from Eq. (4-5) and get the Rutherford cross-section formula

$$\frac{d\sigma}{d\Omega} = \frac{z^2 Z^2 e^4}{64\pi^2 \epsilon_0^2 m^2 v_0^4 \sin^4 \theta/2}. \quad (4-17)$$

The interpretation of this equation is that each nucleus represents a target area $d\sigma$ for deflecting a particle by an angle θ into a solid angle $d\Omega$. Let the target foil have n atoms per unit volume and a thickness Δx , and let the detector be at an angle θ subtending a solid angle $\Delta\Omega$ with the target. By using Eq. (1-35), we find the fraction of alpha particles from the beam scattered to the detector to be

$$\frac{\Delta N}{N} = n \left(\frac{d\sigma}{d\Omega} \right) \Delta\Omega \Delta x, \quad (4-18)$$

with the differential cross section $d\sigma/d\Omega$ given by Eq. (4-17).

Rutherford's formula gives infinite cross section for $\theta = 0$. This corresponds to $b \rightarrow \infty$ and in reality, of course, we do not have infinite impact parameters. Indeed, we could have set an upper limit for b as approximately the radius of the atom, because outside the atom the electric field from the nucleus is shielded by the electrons.

Neglecting the region close to $\theta = 0$, we see that the angular distribution of alpha particles is described by the factor $(\sin \theta/2)^{-4}$. This term does not vary nearly so fast with θ as does Eq. (4-2). Rutherford found that all available data agreed with his predictions and thus was the nuclear model of the atom born. The year: 1911.

In 1913, Geiger and Marsden* published the results of a very exhaustive test of Rutherford's theory. They used silver and gold foils as targets for the alpha particles and recorded the rate of scintillations as a function of angle

* H. Geiger and E. Marsden, *Phil. Mag.* 25 (1913), p. 605.

over a very wide angular range. Fig. 4-3 shows their result. In this graph, according to Rutherford's formula, all points for a given experiment should fall on a straight line with a slope of 45° . The agreement is very good, considering in particular the fact that the counting rate, measured by eye, varied over almost four decades.

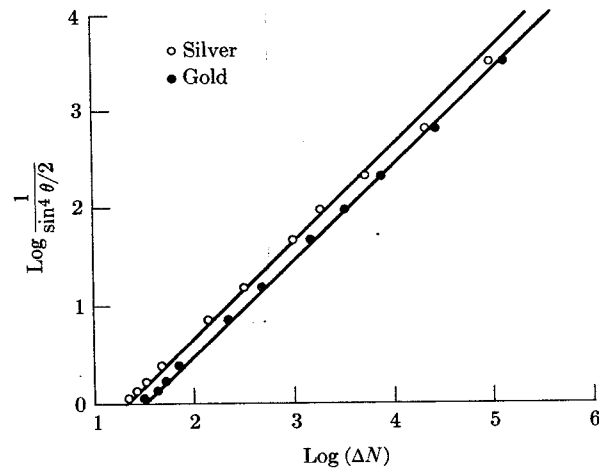


Fig. 4-3 Number ΔN of scattered alpha particles versus scattering angle θ (logarithmic). Reproduced by permission from Richtmyer, Kennard, and Lauritsen, *Introduction to Modern Physics*, New York: McGraw-Hill © 1955, p. 146.

Geiger and Marsden, and later Chadwick, also attempted to measure absolute values for the scattering rate (i.e., the cross section) such that they could thereby determine the nuclear charge Z . They concluded that Z was approximately half the atomic mass number. Much more accurate measurements of Z for a large number of elements were made about this time by Moseley. His experiments with x-rays emitted by the various elements showed that Z is identical with the atomic number; that is, the number giving the place of the element in the Periodic Table. This will be discussed in more detail in Chapter 10.

4-4 SIZE OF THE NUCLEUS

The detailed studies of alpha scattering carried out in Rutherford's laboratory on many elements soon revealed that the simple $(\sin \theta/2)^{-4}$ law does not always hold. The discrepancies occur for light elements, particularly for large angles of deflection. This was immediately interpreted as a breakdown of the r^{-2} force law at small distances. Put differently, it revealed that the nucleus is not a point charge and that at small distances forces other than the Coulomb

force are acting. It was possible to estimate that the radius at which these forces affected the motion of the alpha particles was of the order of 5×10^{-15} m for medium-mass atoms.

We now know that the nucleus consists of protons and neutrons held together by very short-range but very strong forces. An alpha particle approaching the nuclear surface experiences these forces and may be scattered or broken up into its components, two protons and two neutrons. The study of these processes is a part of nuclear physics, discussed briefly in Chapter 12.

4-5 SPECTRA

Most readers of this book have studied light and know that spectrographs are instruments which analyze light according to its distribution of frequency or color. These instruments always have an entrance slit, a dispersive component that may be a prism or grating, and a detector that is usually a photographic plate. The instrument forms an image of the slit on the detector, the focusing being accomplished with a system of lenses, or in the case of a reflective-grating spectrometer by the curvature of the grating. Separated images are formed for each frequency of light present, so that light which is continuous in its frequency distribution forms a wide image that is a continuous succession of slit images. Light which is discontinuous in frequency distribution forms a discrete set of slit images that are called *spectral lines*.

Figure 4-4(a) depicts a reflective grating made by scribing fine lines in a highly reflective metallic surface. A parallel beam of light falling in on the mirror at an angle θ_i with the normal will be reflected—to zeroth order—such that it leaves at an angle θ_r , as shown. A first-order maximum in the diffraction

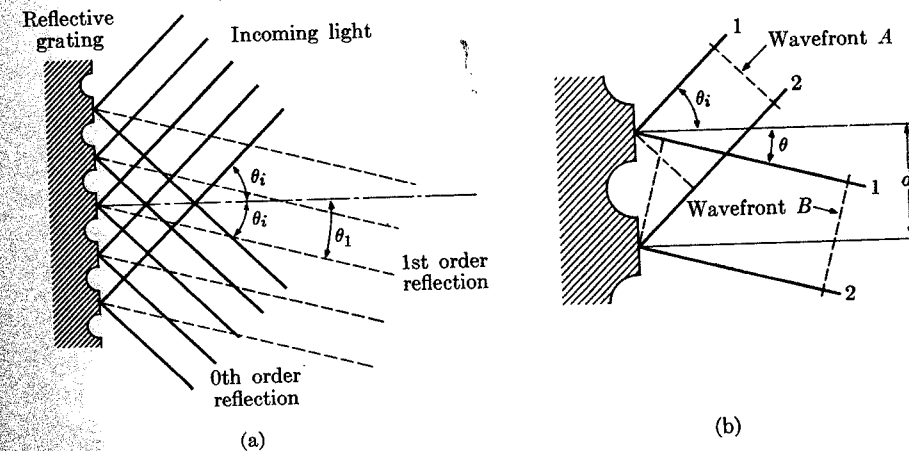


Fig. 4-4 (a) Reflection of parallel light from a grating. (b) Detail of the 1st-order reflection. Path 2 one wavelength longer than 1.

pattern will occur at some angle θ_1 and if the grating has a large number of lines, this maximum will be sharp.

Figure 4-4(b) shows in more detail two rays falling in on the grating. The points where these rays hit the grating are sources of light radiating in all directions. To get constructive interference when the two rays later are focused to one point on the detector, the wave fronts must be perpendicular to the direction of motion. This will be the case if the difference in path length from wave front A to wave front B is a whole number of wavelengths; that is,

$$d(\sin \theta_i - \sin \theta) = n\lambda, \quad (4-19)$$

where n is an integer. For $n = 0$, we get $\theta = \theta_i$, independent of λ . For $n = 1$ or higher, we see that $\sin \theta$ depends on λ . The grating therefore disperses light according to the wavelengths of its components.

Figure 4-5 shows the layout of a concave grating spectrometer. The reflective grating is bent with a radius of curvature $2R$. The entrance slit for the light and detector plates are placed on a circle with radius R . It can then be shown that sharp images of the slit will be produced, by the focusing action of the mirror grating, on the detector.

Spectroscopy with prism spectrometers, as well as with grating spectrometers, was a well-developed science in the latter part of the last century. It was found that the light from any element in gaseous form produces a discontinuous line spectrum. Each element has its own characteristic frequency distribution

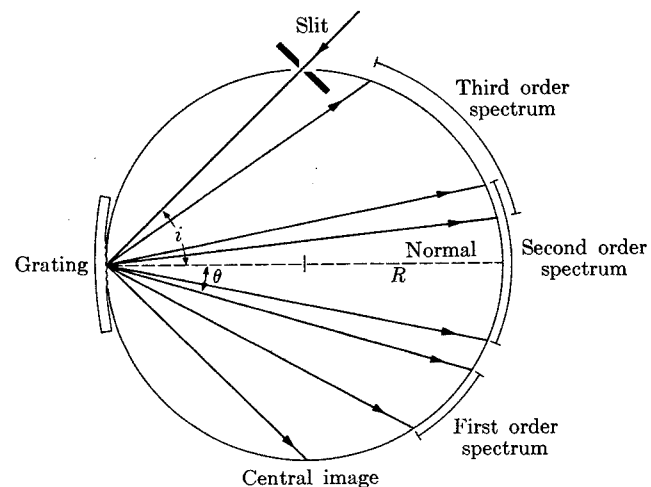


Fig. 4-5 Concave grating spectrometer. Images of the slit are formed on the curved photographic plates by the curvature of the grating (radius $2R$) acting as a concave mirror. Reproduced by permission from Jenkins and White, *Fundamentals of Optics*. New York: McGraw-Hill © 1957, p. 348.

or spectrum, so that each element can be identified by the light that it emits. The most dramatic instance of such identification occurred when the element helium was "discovered" in the spectrum of the sun before it was chemically isolated here on earth.

The emission of a spectral line by gas atoms could presumably be explained somewhat as follows on the basis of the Thomson model of the atom: An electron is bound to the atom by electric and possibly other forces and is normally at rest in an equilibrium position. Displaced from that position by a collision between two atoms it will execute oscillations. Since it is charged, it will radiate energy of frequency equal to the frequency of oscillations. If the oscillations are not strictly harmonic (i.e., proportional to $\sin \omega t$), it will also radiate higher harmonics. The puzzle is that no atom radiates spectral lines with frequencies being simple harmonics of a fundamental. All elements display a great multitude of lines spread over a very large frequency spectrum. Certain regularities are found (next section) but nothing that supports the above picture.

After Rutherford's discovery of the nucleus, it was immediately suggested that the electrons move in orbits about the nucleus and that the electrostatic attraction provided the centripetal force. The difficulty with this model is that the electron is continuously accelerating (centripetal acceleration), and according to classical electromagnetic theory an accelerating charge e radiates power at a rate $P = e^2 a^2 / 6\pi\epsilon_0 c^3$ watts, where a is the acceleration. A simple calculation shows that the electrons in orbits about the nucleus would lose energy and spiral in towards the nucleus so fast that in about 10^{-8} s all matter would have collapsed.

This set the stage for one of the most brilliant natural philosophers of modern times, Niels Bohr (Section 4-7). Before we present his simple, yet revolutionary, theory, we shall discuss in some detail the experimental data on which it was based.

4-6 THE HYDROGEN SPECTRUM

The obvious place to start the study of spectra is with the spectrum of hydrogen. It is not surprising that this lightest element has the simplest spectrum and probably the simplest structure. Part of the hydrogen spectrum is shown in Fig. 4-6. The regularity of these spectral lines is immediately evident, and it appears obvious that there is some interrelationship among them. In 1884, a Swiss high-school mathematics teacher by the name of Balmer took the wavelengths of these lines as a problem in numbers. He set out to find a formula which would show their interrelation. He hit upon a formula which could be made to give these wavelengths very precisely. The Balmer formula is

$$\lambda \text{ (angstroms)} = \frac{3645.6n^2}{n^2 - 4}. \quad (4-20)$$

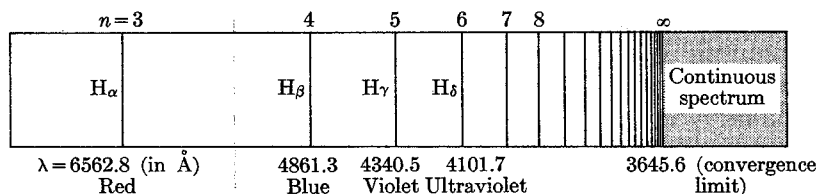


Fig. 4-6 Diagram of the Balmer series of atomic hydrogen. (The wavelengths are the values in air.)

Each different wavelength is obtained by putting into the formula different values of the running integers n , which are $n = 3$, $n = 4$, $n = 5$, etc.

The success of the Balmer formula led Rydberg to attempt a formulation which would apply to heavier elements. He proposed an equation of the form

$$\bar{\nu} = \frac{1}{\lambda} = A - \frac{R}{(n + \alpha)^2}, \quad (4-21)$$

where $\bar{\nu}$ is the *wave number*,* R is the *Rydberg constant* which is equal to $1.09737 \times 10^7 \text{ m}^{-1}$, and n is a running integer. A and α are adjustment constants which depend on the element and the part of the spectrum or spectral series to which the formula is applied. Rydberg found that this formula, which can be regarded as a generalization of the Balmer formula, could be fitted to many spectral series, and further that the value of R was nearly the same when the formula was applied to different elements.

In 1908, Ritz noted that the wave numbers of many spectral lines are the differences between the wave numbers of other spectral lines, and that the A term of the Rydberg formula was really a particular value of a term, like the second term of the Rydberg formula. Using this "combination principle," Ritz rewrote the Rydberg formula as

$$\bar{\nu} = \frac{R}{(m + \beta)^2} - \frac{R}{(n + \alpha)^2}, \quad (4-22)$$

* The wave number $\bar{\nu}$, as used in spectroscopy, is the number of waves per unit length, and differs from the more conventional wave number k used in Chapter 3 by a factor 2π . One might suppose that the logical quantity to use for the reciprocal form of wavelength would be the frequency, c/λ . In spectroscopy, the wave number is used because in order to compute the frequency without losing the remarkable precision of wavelength measurements, it would be necessary to know the velocity of light to an equal precision. Wave numbers can be computed without knowing the velocity of light and so they retain all the accuracy of spectroscopic wavelength measurements. However, the wave number is not an absolute constant for a given spectral line because its wavelength depends upon the index of refraction of the medium in which the measurements are made. The wavelength in air is corrected to vacuum by means of the relation $\lambda_{\text{vac}} = \mu \lambda_{\text{air}}$, where μ is the index of refraction of air for the particular wavelength. In the visible region, λ_{vac} is approximately 2.5×10^{-2} percent greater than λ_{air} .

where α and β are adjustment constants which depend on the element. For different spectral series of a given element, m takes on different integral values. The different lines within a series are computed by changing the running integer n . It is easily shown that when $\alpha = \beta = 0$ and $m = 2$, Eq. (4-22) reduces to the Balmer formula for hydrogen.

In the same year, 1908, Paschen found another hydrogen series of lines in the infrared region to which Eq. (4-22) could be fitted by making $\alpha = \beta = 0$, $m = 3$, and $n = 4, 5, 6$, etc. Thus, both the then-known hydrogen series could be represented by

$$\bar{\nu} = R \left(\frac{1}{m^2} - \frac{1}{n^2} \right). \quad (4-23)$$

This gives the Balmer series when $m = 2$ and $n = 3, 4, 5$, etc., and correctly predicts the Paschen series for $m = 3$ and $n = 4, 5, 6$, etc.

4-7 THE BOHR MODEL AND THEORY OF THE ATOM

Equation (4-23) represented the entire known hydrogen spectrum with great precision, but it was an empirical formula. In spite of many attempts, it defied derivation on the basis of known physical laws. In 1913, Niels Bohr succeeded in deriving this important relation, but only by breaking with concepts of classical physics believed to be well established.

Bohr extended Rutherford's model of the atom. He retained the small core or nucleus of the atom and proposed that the electrons, known to be part of the atom, move in orbits around the nucleus. In the case of hydrogen Bohr proposed that the nucleus consisted of one proton with one electron revolving about it. This is a planetary model of the atom where the heavy positive nucleus is like the sun and the light, negative electron is like the planet earth. In this model, hydrogen is a tiny, one-planet solar system with the gravitational force of the solar system replaced by the electrostatic force of attraction between the oppositely charged particles. The general equations for the gravitational force and the electrostatic force are, respectively,

$$F = G \frac{MM'}{r^2} \quad \text{and} \quad F = \frac{1}{4\pi\epsilon_0} \frac{qq'}{r^2}. \quad (4-24)$$

Both forces are inversely proportional to the square of the distance between the particles. The planets of the solar system have elliptical orbits which are nearly circular. Bohr assumed that the planetary electron of hydrogen moves in a circular orbit, which makes the analysis of the classical aspects of the problem straightforward. Let v be the tangential speed of a mass M' that is revolving around a very large mass M in a circular orbit of radius r . Revolution occurs around the center of mass of the system which, in effect, is at the cen-

of the large, massive body. The centripetal force acting on M' is the gravitational force of attraction due to M . Thus we have

$$F = G \frac{MM'}{r^2} = M'a = \frac{M'v^2}{r}, \quad (4-25)$$

from which we obtain

$$v^2 = \frac{GM}{r}. \quad (4-26)$$

In Bohr's model of the atom, an electron of charge e , mass m_e , and tangential speed v revolves in a circular orbit of radius r around a massive nucleus having a positive charge Ze . In this case, too, the center of the orbit is essentially at the center of the heavy nucleus. The centripetal force acting on the orbiting electron is the electrostatic force of attraction of the nuclear charge, and therefore the force equation is

$$F = \frac{1}{4\pi\epsilon_0} \frac{Ze \cdot e}{r^2} = m_e a = \frac{m_e v^2}{r}. \quad (4-27)$$

From this equation we find that

$$v^2 = \frac{Ze^2}{4\pi\epsilon_0 m_e r}. \quad (4-28)$$

(For hydrogen, the atomic number Z equals one. We include Z for generality.) Each of the equations (4-26) and (4-28) provides a relationship between the variables v and r . If one is known, the other can be found. In the gravitational case, any pair of values of v and of r which satisfy Eq. (4-26) may actually occur. In the electrical case, classical physics imposes no limitation on the number of solutions there can be for Eq. (4-28). For the case of the hydrogen atom, Bohr introduced a restrictive condition which is known as the first Bohr postulate. He assumed that not all the possible orbits that can be computed from Eq. (4-28) are found in hydrogen. Bohr's *first postulate* is that *only those orbits occur for which the angular momenta of the planetary electron are integral multiples of $h/2\pi$, that is, $nh/2\pi$* . Here n is any integer and h is Planck's constant. Bohr's first postulate introduces the integer idea that appears in the Ritz formula and also introduces Planck's constant, which we have seen plays an important role in the atomic view of radiation. Stated mathematically, this first postulate is

$$m_e v r = \frac{nh}{2\pi} = n\hbar, \quad (4-29)$$

where $n = 1, 2, 3, \dots$ and \hbar , called " h -bar" is Planck's constant divided by 2π .

The orbiting electron in hydrogen must simultaneously satisfy the conditions expressed by Eqs. (4-28) and (4-29). After eliminating v between these two

equations, we find that the orbits which exist or are "permitted" in the hydrogen atom are only those that have radii

$$r = \frac{\epsilon_0 h^2 n^2}{\pi m_e Z e^2}. \quad (4-30)$$

With numerical values inserted, this gives

$$r = 0.529 n^2 \times 10^{-8} \text{ m} = 0.529 n^2 \text{ \AA}. \quad (4-30a)$$

Thus, the "first Bohr orbit" has a radius of 0.529 Å; the second has a radius of 2.116 Å, etc.

In discussing the energy of a planetary electron, we shall use the usual convention that the electron has no potential energy when it is infinitely far from its nucleus. The potential energy of a negative electronic charge at a distance r from the nucleus of positive charge Ze is then

$$E_p = -\frac{Ze^2}{4\pi\epsilon_0 r}. \quad (4-31)$$

Note that the potential energy of the electron in this case is zero at infinity and negative elsewhere. We can use Eq. (4-28) to find its kinetic energy:

$$E_k = \frac{1}{2} m_e v^2 = \frac{Ze^2}{8\pi\epsilon_0 r}. \quad (4-32)$$

The total energy of the planetary electron is the sum of the potential and kinetic energies:

$$E = E_k + E_p = \frac{Ze^2}{8\pi\epsilon_0 r} - \frac{Ze^2}{4\pi\epsilon_0 r} = -\frac{Ze^2}{8\pi\epsilon_0 r}. \quad (4-33)$$

We have computed the total energy as a function of r . But we have seen that r can have only those values given by Eq. (4-30). Using this equation to eliminate r , we find that

$$E_n = -\frac{m_e e^4 Z^2}{8\epsilon_0^2 h^2 n^2}, \quad (4-34)$$

where $n = 1, 2, 3, \dots$ for the energy states that it is possible for the electron*

* In calling E the energy of the electron, we are not precise. We have assumed that the electron does all the moving while the nucleus remains at rest. Since the mass M of the proton is 1836 times the mass m_e of the electron, the latter has most of the kinetic energy of the atomic system. A detailed treatment would require us to consider the movement of all particles about their common center of mass. There is a theorem in mechanics which states that in a two-body problem such as this, the motion of one body may be neglected if the mass of the other body is taken to be the "*reduced mass*," which is the product over the sum of the two masses, $m_e M / (m_e + M) = m_e / (1 + m_e/M)$. If, in Eq. (4-34) and elsewhere, we *replace* the electron mass m_e by the reduced mass, then our equations correctly describe the atomic system *as a whole* (Problem 4-7).

to have. The integer n is called the *total* or *principal* quantum number and it can have any of the series of values, 1, 2, 3, The values of n determine the energies of the states. When n is large, the energy is large, that is, less negative than for small integers. The energy required to remove an electron from a particular state to infinity is called the *binding energy* of that state. It is numerically equal to E_n .

Figure 4-7 shows the potential energy and the total energy as a function of r (Eq. 4-33). The allowed orbit radii (Eq. 4-30) are indicated, and the corresponding values of the total energy are shown. The energies are given in electron volts, found by inserting numerical values for the constants in Eq. (4-34) and converting from joules to eV. In general, we get

$$E_n = -\frac{13.6}{n^2} \text{ eV.} \quad (4-34a)$$

We now consider how Bohr used this set of energies to account for the hydrogen spectrum. In Chapter 3 we described how classical electrodynamics predicts that energy will be radiated whenever a charged particle is accelerated. We were careful to point out that the acceleration could be due to a change of direction of motion as well as due to a change of speed. According to classical theory, an orbital electron should radiate energy because of its centripetal acceleration. In order to preserve his atomic model of planetary electron orbits, Bohr had to devise a theory which would violate this classical prediction since, according to it, any electron that separated from the nucleus would soon radiate away its energy and fall back into the nucleus. Bohr's second break with classical physics is contained in his *second postulate*, which states that *no electron radiates energy so long as it remains in one of the orbital energy states*;

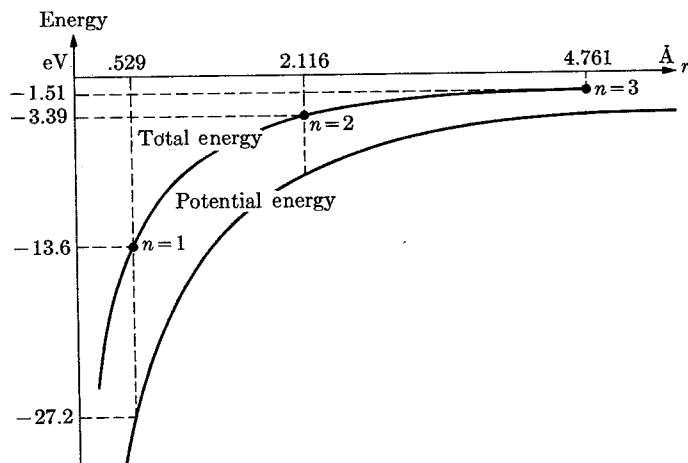


Fig. 4-7 Energy relations in the hydrogen atom.

and that radiation occurs only when an electron goes from a higher energy state to a lower one, the energy of the quantum of radiation, $h\nu$, being equal to the energy difference of the states. Let the quantum number $n = n_2$ represent a higher energy state and $n = n_1$ represent a lower energy state ($n_1 < n_2$), then the second Bohr postulate can be written as

$$h\nu = E_{n_2} - E_{n_1}. \quad (4-35)$$

Substituting for the energies from Eq. (4-34), we have for the frequency of the emitted radiation

$$\nu = \frac{m_e e^4 Z^2}{8\epsilon_0^2 h^3} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \quad (4-36)$$

or, in terms of the wave number,

$$\bar{\nu} = \frac{1}{\lambda} = \frac{\nu}{c} = \frac{m_e e^4 Z^2}{8\epsilon_0^2 h^3 c} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \quad (4-37)$$

where c is the speed of light in a vacuum. Comparing Eq. (4-37) with Eq. (4-23) shows that both have the same form.

Equally impressive is the fact that the constant factor of the Bohr formula is the Rydberg constant, R . Again comparing Eqs. (4-37) and (4-23), we find that, since $Z = 1$ for hydrogen,

$$R = \frac{m_e e^4}{8\epsilon_0^2 h^3 c} = 1.0973731 \times 10^7 \text{ m}^{-1}. \quad (4-38)$$

The R given here is R_∞ , which would be correct if the mass of the nucleus were infinite compared with the mass of an electron. If the motion of the nucleus is taken into account, m_e must be replaced by the reduced mass. Therefore, in general, $R = R_\infty / (1 + m_e/M)$. This accounts for the slight variation of R from element to element noted by Rydberg. It is a triumph of the Bohr model and theory that the slight differences between the spectra of ordinary hydrogen and its isotope, heavy hydrogen (deuterium), can be attributed to the influence of the nuclear mass. In fact, heavy hydrogen was discovered spectroscopically by Urey in 1932.

The Bohr formula gives the Balmer series for $n_1 = 2$ and the Paschen series for $n_1 = 3$, as we have seen before. But the Bohr theory places no restrictions on n_1 and his result suggested that there might be additional hydrogen series not yet found experimentally. In 1916 Lyman found a series in the far ultraviolet, in 1922 Brackett found a new series in the infrared, and in 1924 Pfund located another in the same region. Table 4-1 summarizes the five hydrogen series.

Table 4-1 The spectral series of hydrogen

Values of n_1	Name of series	Values of n_2
1	Lyman	2, 3, 4, etc.
2	Balmer	3, 4, 5, etc.
3	Paschen	4, 5, 6, etc.
4	Brackett	5, 6, 7, etc.
5	Pfund	6, 7, 8, etc.

4-8 HYDROGEN ENERGY LEVELS

The discovery of sharp energy states of the hydrogen atom was a finding that had very far-reaching consequences in physics. All atomic, molecular, and nuclear systems have discrete energy levels; indeed, macroscopic systems can exist only in states of discrete energies, but these energy levels are so closely spaced that they cannot be experimentally resolved. Because of the general interest of this subject, we shall here look at the energy levels of hydrogen in some detail.

These levels can be represented graphically as shown in Fig. 4-8. The quantum numbers are shown at the left and the corresponding energies of hydrogen in electron volts are given at the right. In this array of energies, the higher (less negative) energies are at the top, while the lower (more negative) are toward the bottom. In a normal unexcited hydrogen atom, the electron is in its lowest energy state at the bottom, with $n = 1$. An electron in this *ground state* is stable and remains in this state continuously without emitting or absorbing energy. The "excitement" begins when the electron absorbs energy in some way. There are a variety of ways in which this may be brought about. If the hydrogen is in an electric discharge, a free electron which has been accelerated by the electric field may hit* it. If the hydrogen is heated, the electron may be excited by a thermal-motion collision. If the hydrogen is illuminated, it may absorb energy from a photon. Suppose the electron in hydrogen absorbs about 20 eV of energy in one of these ways. This is enough energy to lift the electron to $n = \infty$ (13.6 eV) with 6.4 eV left over. In this case, the electron is made entirely free of its home nucleus and is given 6.4 eV of kinetic energy besides. If the electron absorbs just 13.6 eV, it is merely freed from its home nucleus and drifts about with only its thermal kinetic energy. In either of these cases the remaining nucleus is an ion. If the energy of a bombarding electron is less than that required for ionization but equal to or

* We use the word "hit" loosely. We saw in the discussion of alpha-particle scattering that a collision between charged bodies does not involve physical contact in the usual sense.

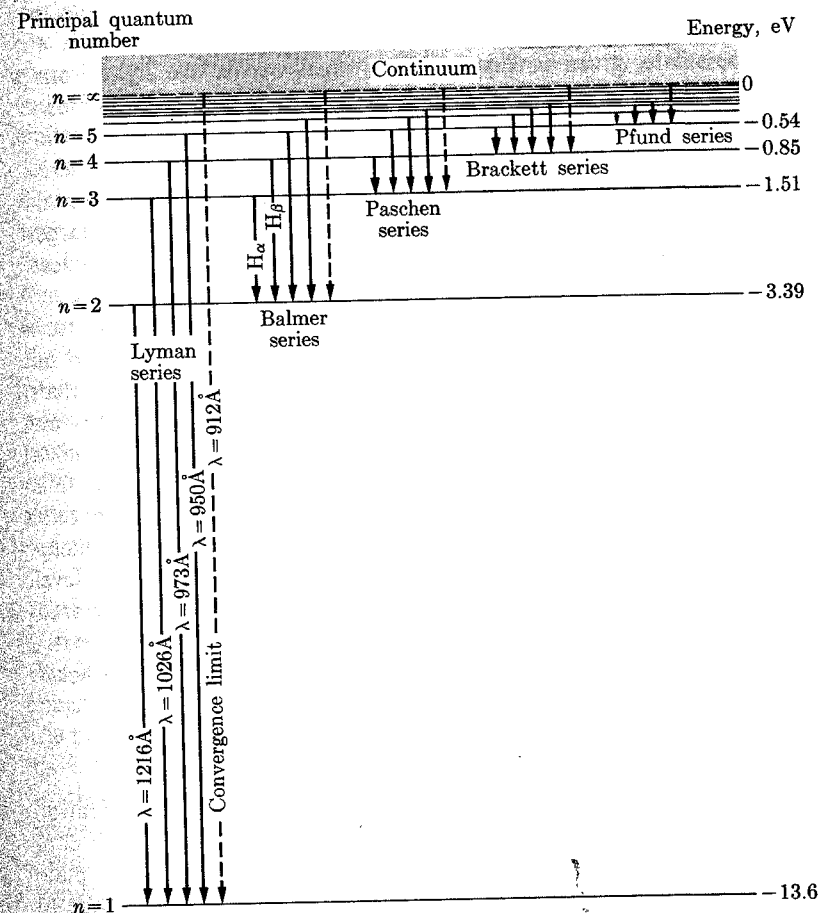


Fig. 4-8 Energy-level diagram of the hydrogen atom.

greater than that needed to raise an electron in an atom to one of its permitted energy levels, then the atomic electron will absorb just enough energy to put it into some higher energy state. After the bombarding electron has transferred enough energy to the atom to excite it, the electron will leave the encounter, carrying away any excess as kinetic energy. The *excitation energy* of any level in electron volts is *numerically* equal to the *excitation potential* of that state in volts.

After excitation, the atomic electron returns to its normal state. If it was excited to $n = 4$, it may jump from 4 to 1 in one step. It may also go 4, 2, 1 or 4, 3, 1 or 4, 3, 2, 1. In each step of the return trip, the electron must lose an amount of energy equal to the difference of the energy levels. The only

mechanism available for this energy loss is through the emission of electromagnetic radiation. Thus, in Fig. 4-7 we have represented graphically the second Bohr postulate, given in Eq. (4-35). When we see the light from a hydrogen discharge, we are "seeing" the electrons go from excited states to lower states.

The electron transitions which end on $n = 1$ constitute the Lyman series, on $n = 2$, the Balmer series, on $n = 3$, the Paschen series, etc. From the energy-level diagram we can see that the Lyman transitions involve the largest changes of energy, produce the highest frequencies, and provide the "bluest" (ultraviolet) light.

The shaded region at the top of Fig. 4-7 represents the fact that electrons at infinity may have kinetic energy, so that their energy there is not zero but positive. If the electron of hydrogen is completely removed from its nucleus, then one of these electrons at infinity having *any* energy may fall into any one of the energy levels. Such an electron undergoes a change of energy equal to its energy at infinity minus the negative energy of the level to which it falls. The "double negative" in the last sentence enables us to conclude that the energy radiated by such a transition is the sum of the electron's kinetic energy at infinity and that involved in the transition from $n = \infty$ to the final level. The energy radiated will have a value greater than that involved in the transition from $n = \infty$ to the final level. Since there is a wide distribution of the energies among the electrons at infinity, there is a continuous spectrum below the short-wavelength convergence limit of any series.

4-9 IONIZATION POTENTIALS

Confirmation of the energy level concept is convincingly given by a consideration of ionization potential. Consider first a radio-type tube, Fig. 4-9, which contains only a filament-heated cathode and a plate as anode. When the plate is positive with respect to the cathode, electrons will move across the tube to the anode. This current is limited by two factors. First, the number of electrons emitted per unit area from a cathode depends upon cathode composition and temperature. In the remainder of this discussion we shall assume that the cathode is operated hot enough so that the tube current is not significantly limited by cathode emission. The second factor is the effect of the electrons

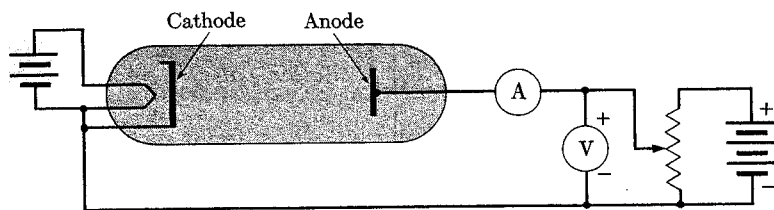


Fig. 4-9 Apparatus for determining ionization potential.

in the region between the electrodes upon those emerging from the cathode. The concentration of negative charge in the inter-electrode region is called *space charge*, and it lowers the potential in the vicinity of the emitting surface. Indeed, the potential in this region usually falls below the potential of the emitter. Thus, although the plate or accelerating potential is still positive, this decrease in potential due to space charge will reduce the electron current because the potential barrier will turn back electrons emitted with low kinetic energy. (The electrons in thermionic emission have a distribution of speeds similar to that of the molecules of a gas.) However, those high-energy electrons that get beyond this barrier caused by space charge arrive at the plate with the same energy they would have had if the space charge had been absent, since the total potential difference V between the electrodes is independent of the space charge. The space charge limited current is not a linear function of the potential difference as in the case of an ohmic resistor; it is found to be proportional to the three-halves power of the potential difference. This is known as the Child-Langmuir Law. In mathematical form, it is $I = kV^{3/2}$. The value of k depends upon the geometry of the tube and the volume density of the charges between the electrodes.

The ionization potential of a gas is determined by introducing some of the gas into a tube such as that shown in Fig. 4-9, and then measuring the plate current as a function of plate voltage. As the potential difference is increased, it is found that above some particular value of the potential the current increases much more rapidly than it does below that value, as shown in Fig. 4-10. When the plate potential reaches this critical value, the electrons arriving at the anode have acquired enough energy to knock electrons off the atoms of the gas close to this electrode. The positive ions produced when the voltage equals or exceeds the critical value neutralize some of the negative space charge. Thus ionization causes a marked increase in the tube current. If the gas under study is hydrogen, the ionization potential is found to be 13.6 V. It is a remarkable confirmation of the energy-level idea that there should be excellent agreement

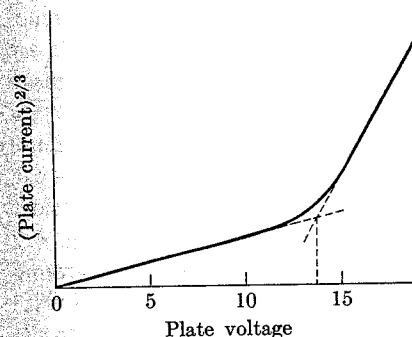


Fig. 4-10 Plate current in hydrogen-filled tube.

for the ionization potential as measured by the very different techniques of spectroscopy and electronics. Since the electrons are emitted from the cathode with an initial velocity distribution, some of them acquire enough energy to produce ionization at lower accelerating potentials than others. This accounts for the curved section joining the two straight-line portions of the graph in Fig. 4-10. Except for this short curved part, the break in the line is quite abrupt. This sudden change of slope would not occur if several low-energy electrons could combine in their "efforts" to ionize the atom of hydrogen.

4-10 RESONANCE POTENTIALS

The experiment just described was set up to measure the potential through which electrons must be accelerated before they can lift orbital electrons from their lowest energy state (ground state) to infinity. This ionization was detected by an increase in the current through the tube. But before the bombarding electrons have enough energy to take the atom apart by removing an electron, they have enough energy to lift an electron to an excited state. Orbital electrons in the gas can be transferred from their lowest energy state to any of the higher states. As implied earlier, the quantum conditions which require an orbital electron to emit only certain frequencies as radiation apply also to the absorption process. These electrons can absorb only energies represented by transitions between energy levels. If an orbital electron is hit by a bombarding electron with insufficient energy to produce an energy transition, the orbital electron absorbs no energy from the bombarding electron and *the collision is perfectly elastic*. If the orbital electron is hit by a high-energy bombarding electron, then the orbital electron can absorb energy by making a transition. This leaves the bombarding electron with that much less energy. *Such a collision is inelastic*, since the bombarding electron is left with less energy than it had before the collision. Such an inelastic collision puts the orbital electron in one of the excited states, and hence it can radiate energy in returning to a lower state.

Consider again the ionization experiment. As the potential difference across the tube is slowly increased, the electrons from the heated cathode are accelerated to higher and higher velocities. At low speeds, these electrons make completely elastic collisions with the electrons of the gas, so that they are deviated but not slowed by the collision process. As the potential difference across the tube is increased, however, a potential is reached where energy can be transferred to an orbital electron. For the purpose of discussion consider hydrogen, which has an ionization potential of 13.6 V. A look at Fig. 4-8 discloses that the least amount of energy the orbital electron in the ground state can absorb is $13.6 \text{ eV} - 3.4 \text{ eV}$ or 10.2 eV . A bombarding electron with 10.2 eV of energy can "resonate" with hydrogen and transfer its energy to the hydrogen. This produces no ionization, so the current through the tube is not

changed, but after making such collisions, the bombarding electrons proceed more slowly and the hydrogen shows its "excitement" by radiating. The hydrogen will not glow visibly because this resonance radiation is one line of the Lyman series, which is in the ultraviolet region; however, ultraviolet spectroscopy confirms that the radiation is there.

In order to demonstrate the resonance phenomenon electronically, we need a more elaborate tube, such as that used by Franck and Hertz,* who first performed the experiment in 1913 using mercury vapor as the gas. Mercury has 80 electrons around its nucleus and has therefore a much more complex energy-level diagram than hydrogen. The important fact, however, is that it, like hydrogen, has discrete energy levels to which the atom can be excited by electron bombardment. Mercury vapor is chosen because it is monatomic whereas hydrogen is ordinarily a diatomic molecule whose dissociation energy is 4.5 eV . If the gas were hydrogen, most of the bombarding electrons would give up their energy to excite molecular energy states and also to dissociate the molecules after the accelerating potential reached 4.5 V . This complex situation would conceal the effects of atomic hydrogen in this type of experiment.

The principal parts of such a tube are shown schematically in Fig. 4-11. From the standpoint of electronics, the effect of resonance is that the bombarding electrons are slowed down, so we need a device which will measure the energy of the bombarding electrons after they have made collisions. Suppose that the anode of the ionization tube is perforated or made of wire mesh. In this case, some of the bombarding electrons will pass through the electrode rather than hit it. We now need to know the energy with which the bombarding electrons arrive at the anode.

In our consideration of the photoelectric effect, we measured the energy of photoelectrons by making them move against the force action of an electric field, and the energy of the photoelectrons was given by the stopping potential. Here we use much the same technique and insert into the tube another electrode beyond the anode. This collector electrode is maintained less positive than the

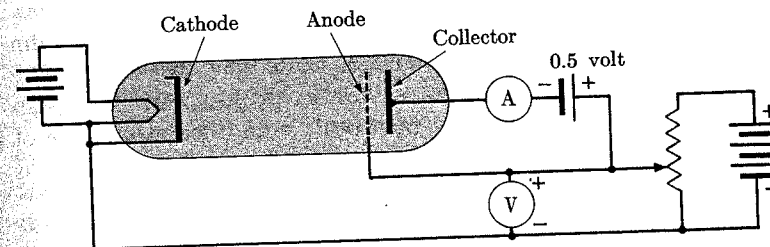


Fig. 4-11 Apparatus for determining resonance potential of gas.

* J. Franck and G. Hertz, *Verhandl. Deut. Phys. Ges.* **16** (1914), p. 512.

anode, say 0.5 V, so that any electrons that pass through the anode will be slowed by the field between the electrodes. Electrons which reach this last electrode must have passed the anode with an energy of at least 0.5 eV.

The experimental procedure consists of measuring the collector current as a function of the anode potential with respect to the cathode, and typical results are shown in Fig. 4-12. From $V = 0$ to $V = 0.5$ V, there is no collector current, since no electrons can reach the anode if they have less than 0.5 eV of energy. Above $V = 0.5$ V, the collector current rises because the number of electrons having at least this minimum energy increases. When V reaches the 4.9-eV resonance potential of the gas, the collector current begins to decrease because some of the bombarding electrons are slowed by inelastic collisions with orbital electrons in the gas. The current rises again as V is further increased since, in the stronger field, bombarding electrons can make inelastic collisions early and still undergo enough acceleration to surmount the 0.5-V barrier.

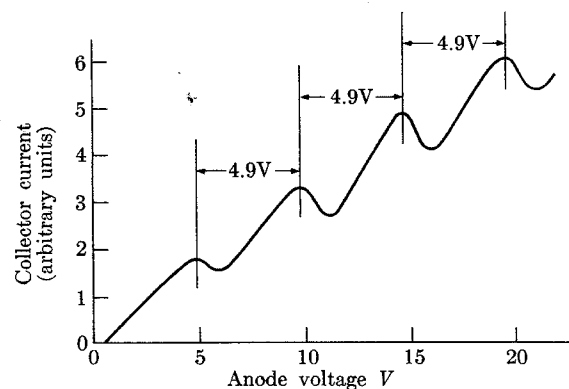


Fig. 4-12 Resonance potential curve for mercury.

The second dip is not due to a new energy transition, because very few electrons ever get enough energy to excite the next transition. The second dip occurs at twice the resonance potential and is caused by the bombarding electrons suffering two inelastic collisions of the same kind. Thus each peak of the curve signifies more collisions and each peak is an integral multiple of the resonance potential. The separation of successive resonance peaks is 4.9 V for mercury*.

* Since mercury ionizes at 10.4 V, the third resonance peak will be masked by other effects if the tube shown in Fig. 4-11 is used. Actually, a more complicated tube which differentiates the resonance and ionization effects is used. This important experimental detail does not in any way alter the principle discussed in this section.

Franck and Hertz studied the radiation given off by the mercury vapor bombarded by the electrons and found a well-known mercury line at $\lambda = 2537$ Å. The corresponding photon energy is given by Eq. (3-47) as

$$E = \frac{1.24 \times 10^4}{2537} = 4.9 \text{ eV}.$$

The radiation from the mercury vapor was detected only when the anode voltage exceeded 4.9 V. Clearly, the energy level in mercury at 4.9 eV cannot be excited by multiple hits from electrons; it has to be reached in one single step. This is clear evidence that mercury cannot exist with an intermediate energy content and is the strongest proof yet devised of Bohr's idea of discrete levels.

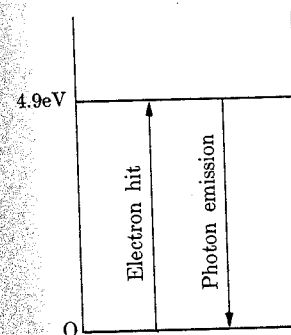


Fig. 4-13 Energy-level diagram illustrating absorption and emission of energy by mercury.

Figure 4-13 shows the ground state and first excited state of mercury in an energy-level diagram where the ground-state energy has been chosen as reference. The absorption and emission processes of the Franck-Hertz experiment are indicated by arrows.

4-11 PHOTON ABSORPTION

In the previous two sections we have discussed how an atom can absorb discrete amounts of energy from bombarding electrons. An atom may also absorb energy from photons, but there is an important difference. Absorbed photons disappear entirely. A photon with more energy than the ionization energy of an atom can always be absorbed because the excess energy will appear as kinetic energy of the photoelectron. A photon with less than the ionization energy cannot be absorbed unless its energy is equal to one of the

excitation energies of the absorbing atom.* Consider hydrogen again. Ordinarily, the probability of finding a hydrogen atom in an excited state is very small; therefore, we assume that it is always in its ground state. Thus hydrogen can *only* absorb photons whose wavelengths correspond to those emitted in the far ultraviolet, the Lyman series. Hydrogen atoms are therefore transparent to visible and infrared light. If we pass radiation of all wavelengths through hydrogen and analyze the transmitted light by means of a spectrograph, we find the transmitted intensity *reduced* for the Lyman wavelengths. Such a spectrum, having a bright background and *dark lines*, is called an *absorption spectrum*. Because the atoms that have been excited by the absorption of radiation re-emit photons in *random* directions upon returning to the ground state, there is a decrease of intensity along the direction of the transmitted radiation. The absorption lines observed are actually very faint bright lines that appear dark by contrast.

There are certain advantages of studying absorption spectra. For many atoms, as for hydrogen, the absorption spectrum is simpler than the emission spectrum. For hydrogen, as mentioned above, one can observe absorption for the Lyman series only. From these lines, one can directly construct an energy-level diagram. According to our present simple theory, this energy-level diagram appears to be complete. It is not, because selection rules (see below) do not allow absorptive transitions to all states, in particular for many-electron atoms. However, absorption spectra give the most direct information on the levels that do connect with the ground state by photon emission or by absorption.

The determination of elements on the sun is a dramatic example of absorption spectroscopy. The sun is a hot body which emits a continuous spectrum of photons. As these photons pass through the outer atmosphere of the sun, wavelengths which are characteristic of the gases present are absorbed. Thus the continuous spectrum of the light from the sun is crossed with (relatively) dark lines which were first observed by Fraunhofer in 1815. Most of the Fraunhofer lines correspond to the wavelengths of elements found on the earth. The absorption lines of the Balmer series of hydrogen are especially prominent in the spectrum of the sun. The Balmer lines of hydrogen and the visible-region lines of other elements have rather long wavelengths and can be absorbed *only* by excited atoms of the respective elements. These higher energy states are produced in the following way. Although the gaseous atmosphere of the sun is cooler than its surface, the temperature of the gas is still so high that a large number of atoms have sufficient kinetic energy to excite

* This statement is only approximately true. First, an excited state has a certain width, so that the energy of the incident photon can vary within some narrow limits, and absorption still takes place (see Chapter 8). Secondly, in a process called the Raman effect, a photon of energy higher than a given energy level can with finite but low probability excite the atom to that state, with the excess energy being carried off in the form of a reduced-energy photon.

many other atoms by collision. Thus these atoms are raised above the lowest energy level to states where they can absorb wavelengths longer than the ultraviolet. For many years one set of Fraunhofer lines in the visible region could not be associated with any known element. It was presumed to be due to a new "sun element" which was appropriately named helium. This hypothesis was confirmed when helium was isolated on the earth and its emission spectrum was found to correspond with the previously unidentified Fraunhofer lines.

Many of the spectral series that are characteristic of molecular structure are in the infrared region. Absorption spectroscopy is the only feasible way of investigating the structure of these molecules that would be dissociated by being excited in an electric arc in an attempt to produce emission lines. Molecular spectra are further discussed in Chapter 11.

4-12 A CRITICISM OF BOHR'S THEORY

Max Planck discovered that energy was exchanged between a heated body and the surrounding electromagnetic field in quantized steps. Niels Bohr discovered quantization of angular momentum and quantization of the energy content of the atom. He interpreted the observed discrete frequencies of emitted radiation as arising from "quantum jumps" between discrete atomic energy levels with the frequency ν given by $h\nu = \Delta E$. Bohr's theory, or parts of it, has been superseded by *wave mechanics*, in which the quantization of angular momentum and energy is shown to result from the wave nature of matter. The principal shortcomings of Bohr's theory are the following:

1. The emission spectrum from the hydrogen atom exhibits more details, i.e., splitting of the lines, when recorded in a spectrograph with high resolving power. By assuming elliptic orbits in addition to circular ones, and by separately quantizing the angular motion and the radial motion, Sommerfeld* contributed substantially to the resolution of this problem. Uhlenbeck and Goudsmit† postulated that the electron has an intrinsic angular momentum, called the *spin* of the electron. With these modifications, Bohr's theory comes close to predicting the exact position of the energy levels of the hydrogen atom. However, modern precise measurements show discrepancies and can only be explained by a refined theory of wave mechanics (see Chapter 7 and the references given there).

2. The quantization of the angular momentum, $mvr = n\hbar$ of an individual electron applies only if the electron moves in a pure central-force field. This is not the case when there is more than one electron in the atom because of the mutual repulsion between them. Therefore Bohr's theory is strictly a

* A. Sommerfeld, *Ann. Physik* **51** (1916), p. 1.

† G. E. Uhlenbeck and S. A. Goudsmit, *Naturwiss.* **13** (1925), p. 593.

one-electron theory, although most of the concepts are valid also for many-electron atoms. Wave mechanics applies equally well to any atom or molecule. However, mathematical complexities make it difficult in practice to calculate with precision anything more complex than the structure and energy levels of the helium atom (see Chapter 9).

3. The quantum jumps were introduced by Bohr as a postulate. Using the refined theories of Sommerfeld and others, it was also found that quantum jumps occurred from a given level only to certain selected other levels. *Ad hoc selection rules* were found, but not in any way understood. There was no way of calculating or even of estimating the length of time an electron would stay in a given orbit. All this was resolved very naturally by wave mechanics (see Chapter 8).

After studying wave mechanics of the hydrogen atom, the student will realize that Bohr's picture of it is too naïve, and that some of his ideas will have to be discarded (notably the sharp orbits). Some purists with the hindsight of wave mechanics call Bohr's theory a "historic accident". Most physicists, however, agree that Bohr laid the foundation for the theory of the atom.

PROBLEMS

- 4-1 Assuming that the nucleus has a well-defined spherical boundary, find the electric-field intensity at the surface of a) a hydrogen nucleus which has a radius of 0.8×10^{-15} m, and b) a gold nucleus which has a radius of 7.0×10^{-15} m.
- 4-2 An alpha particle having a kinetic energy of 7.68 MeV is projected directly toward the fixed nucleus of a copper atom. What is their distance of closest approach?
- 4-3 a) Calculate n , the number of atoms per unit volume for aluminum and for gold. (The relative densities for aluminum and for gold are 2.70 and 19.3, respectively.) b) When a parallel beam of 4.80-MeV alpha particles is incident normally on gold foil having a thickness of 4.0×10^{-15} cm, then 2.0×10^4 particles per second are recorded by a detector at 20° . How many will be recorded at 60° ? c) How many would be recorded at 20° if the alpha-particle energy were reduced to 2.40 MeV? d) How many would be recorded at 20° if the initial beam of 4.80-MeV alpha particles had been incident on aluminum foil having a thickness of 6.0×10^{-5} cm instead of on the gold foil?
- 4-4 a) The probability that a stream of particles will be scattered through an angle θ or more is equal to the ratio of N_θ , the number of such scattered particles, to N , the total number of incident particles. a) Show that when a beam of particles having kinetic energy E_k undergoes Rutherford scattering in a piece of foil Δx thick and containing n nuclei per unit volume,

$$N_\theta N = \sigma n \Delta x = \pi b^2 n \Delta x = \pi \left(\frac{1}{4\pi\epsilon_0} \frac{zZe^2}{2E_k} \cot \frac{\theta}{2} \right)^2 n \Delta x.$$

- b) What is the impact parameter when a 4.80-MeV alpha particle is scattered 20° by a gold nucleus and when it is scattered 60° ? c) If a piece of gold foil is 4×10^{-5} cm thick, what fraction of a beam of 4.80-MeV alpha particles can be expected to be scattered more than 20° and more than 60° ?
- 4-5 A narrow parallel beam of 4.80-MeV alpha particles striking a copper foil (density 8.9) 10^{-4} cm thick has an intensity of 10^6 particles per second. How many scintillations per minute will be produced by those scattered particles striking a 2 mm \times 2 mm fluorescent screen which is 5 cm away from the point of incidence in a direction of 60° with the line of incidence?
- 4-6 a) Calculate the radii of the first, second, and third "permitted" electron orbits in hydrogen in Ångströms. b) What is the diameter of the hydrogen atom in the ground state? c) Calculate the electric-field intensity at the first orbit due to the nuclear charge and compare the result with the answer to Problem 4-1.
- 4-7 Repeat the calculations of Eqs. (4-27) to (4-34), taking into account the finite proton mass; i.e., use the center of mass as center of rotation for the electron. In rewriting Eq. (4-29), note that the sum of the angular momenta of the two particles is $n\hbar$.
- 4-8 The Bohr model for hydrogen shows that the orbital electron can be found only at certain fixed distances from the proton, the larger radii corresponding to higher quantum numbers. Assume that the electron in a hydrogen atom moves outward to larger radii. Which of the following quantities increase and which decrease: angular momentum, total energy, potential energy, kinetic energy, frequency of rotation?
- 4-9 A particle of mass m moves in a circular orbit of radius r under the influence of a "spring" force kr directed toward the center (k is a constant). Assuming that Bohr's postulates apply to this system, derive the equation for a) the radii of the permissible orbits and b) the energies of these orbits in terms of the quantum number n . c) Show that the frequency radiated when the particle makes a transition from one orbit to the adjacent orbit is the same as the frequency of the circular motion.
- 4-10 Calculate the binding energy of the electron in hydrogen in joules and in eV when $n = 1, 2, 3$, and infinity.
- 4-11 Rearrange and alter the Balmer formula, Eq. (4-20), so that the left-hand side is wave number in reciprocal meters. Show that the result agrees with Eq. (4-37) when the Rydberg constant is substituted in the latter equation and when $n_1 = 2$ and $n_2 = n$.
- 4-12 Calculate a) the frequency, b) the wavelength, and c) the wave number of the H_β -line of the Balmer series of hydrogen. This line is emitted in the transition from $n_2 = 4$ to $n_1 = 2$. Assume that the nucleus has infinite mass.
- 4-13 An atom of tungsten has all of its electrons removed except one. a) Calculate the ground-state energy for this one remaining electron. b) Calculate the energy and wavelength of the radiation emitted when this electron makes a downward transition from $n = 2$ to $n = 1$. c) In what portion of the electromagnetic spectrum is this photon?

Waves and Particles

5-1 WAVE-PARTICLE DUALITY OF LIGHT: COMPTON SCATTERING

Electromagnetic radiation, which includes visible light, infrared and ultraviolet radiation, x-rays, and the gamma rays emitted by nuclei, is shown to be a wave motion by interference experiments. This type of experiment, which involves constructive and destructive interference, is considered to be a test for the existence of waves since interference patterns produced exhibit maxima and minima exactly as predicted by addition of two sinusoidal amplitudes with varying phase shift. It is difficult to conceive of a mechanism whereby particles without an associated wave nature could produce such results.

On the other hand, a host of experiments indicate that electromagnetic radiation behaves like corpuscles. The classical example that we have already studied is the photoelectric effect (Section 3-11). We shall now discuss an experiment in which electromagnetic radiations, in this case x-rays, behave both like waves and particles. The origin of and the techniques for producing x-rays are treated in Chapter 10 of this book. We shall therefore not go too deeply into the details of the experimental setup here.

The experiment to be discussed was performed by A. H. Compton* in 1923. An outline of the principle is shown in Fig. 5-1. X-rays, that is electromagnetic radiations, of a wavelength of $\lambda = 0.71 \text{ \AA}$ fall in from the left on a carbon target. The radiation scattered from the target at a scattering angle α is analyzed by a spectrometer. This spectrometer works on the same principle as a grating used in spectroscopy of visible light or ultraviolet (see Section 4-5), but because of the very short wavelength of x-rays it is impossible to scribe a grid fine enough to yield an appreciable deflection of the first-order maximum. Therefore, the grating is a crystal, and the regular lines of atoms in the crystal lattice replace the scribed lines of the grating. This will be discussed further in Chapter 10.

* A. H. Compton, *Phys. Rev.* **21** (1923), p. 715; **22** (1923), p. 409.

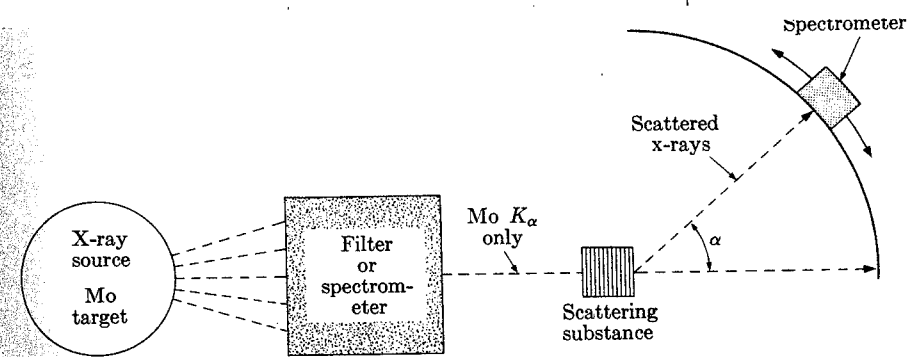


Fig. 5-1 Schematic diagram of the apparatus for measuring Compton scattering.

Figure 5-2 shows the result of Compton's experiment. The top peak at $\alpha = 0$ shows essentially the spectrum of the beam of light incident on the carbon target. It is virtually unchanged by passing through the target. At other scattering angles, we see the appearance of two peaks in the spectrum. One is called the unmodified line, having the same wavelength as the incident radiation; the other peak, which is broader, is called the modified line. It has a wavelength that is larger than that of the unmodified line, and the wavelength increment is increasing with increasing scattering angle α .

The unmodified peak is easy to understand in terms of classical electrodynamics. This classical viewpoint is as follows. The electromagnetic field will exert forces on the charged particles of the atom and thereby perturb the electron orbits. The perturbations have to oscillate with the frequency of the driving force, that is, the frequency of the incident radiation. The oscillations of the electrons will, in turn, produce new electromagnetic radiation going out essentially in all directions, but with an intensity distribution similar to that from an antenna. Unless the incident radiation is polarized, however, this intensity distribution will not be observed. The frequency of the x-radiation of the wavelength used by A. H. Compton in his experiment is much higher than the orbital frequency of the electron in the carbon target. It is then possible to calculate the dynamics of the problem and the energy radiated by the electrons by considering them free particles. Since each electron in this way absorbs a certain amount of energy from the incident x-ray beam, it can be represented by a cross section. The scattering of x-rays without change of wavelength is called *Thomson scattering*, and the cross section referred to is the Thomson cross section. The calculation of this cross section for one "free" electron is rather straightforward and is left to one of the problems (problem 5-1). The result is

$$\sigma_T = \frac{e^4}{6\pi\epsilon_0 m_e^2 c^4} = 6.66 \times 10^{-25} \text{ cm}^2. \quad (5-1)$$

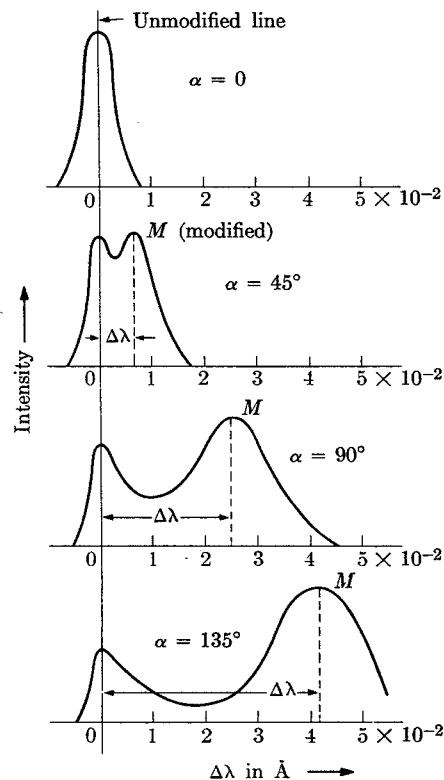


Fig. 5-2 Wavelength displacement of the modified line, M , of the K_α -radiation of molybdenum scattered from carbon, as a function of scattering angle.

This represents the target area for removal of energy from the electromagnetic wave by one electron. The cross section for one atom is simply Z times the one-electron cross section.

The unmodified peaks shown in Fig. 5-2 can be explained as discussed above without resorting to the concept of photons as carriers of the electromagnetic radiation. In the classical picture of the process outlined above, it is clear that an electron in forced oscillations by an external sinusoidal force can only reradiate the same frequency as the incident radiation. From where then do the modified peaks in Fig. 5-2 arise? Compton showed that the *corpuscular* theory of x-rays could explain this peak, and the scattering with modified wavelength is called *Compton scattering*. We shall proceed to calculate the wavelength of the modified peak by assuming that a photon collides elastically with a free electron at rest.

Figure 5-3(a) shows schematically a photon with energy $h\nu_0 = hc/\lambda_0$ approaching an electron at rest. The photon collides with the electron, and

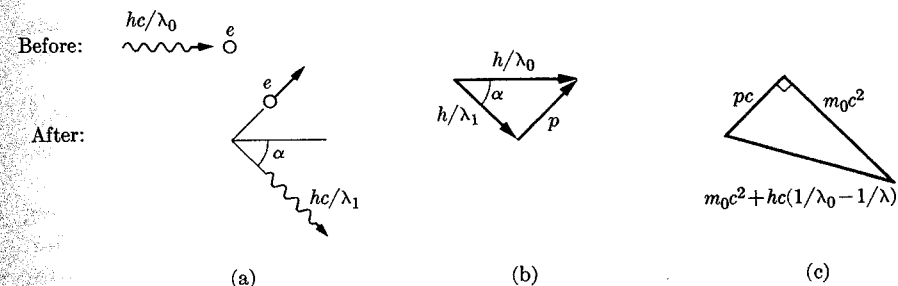


Fig. 5-3 (a) Compton scattering schematic. (b) Conservation of momentum. (c) Mnemonic triangle for electron.

after the collision the photon has been deflected by an angle α . It has given up some of its energy to the recoil energy of the electron, and therefore the frequency has been reduced to $h\nu_1 = hc/\lambda_1$. Figure 5-3(b) shows a triangle which illustrates the conservation of momentum. The photon is here treated as a relativistic particle with zero rest mass. Equation (A3-48) in Appendix 3 then gives for the momentum $p = E/c$. The same relationship between energy and momentum of an electromagnetic wave can be calculated from classical electrodynamics. With $E = h\nu$, we get $p = h\nu/c = h/\lambda$. The momentum of the incident photon is therefore h/λ_0 , and the momentum of the scattered photon is h/λ_1 . Finally, p is the momentum of the electron. Figure 5-3(c) shows a mnemonic triangle for the electron similar to Fig. A3-5. The total energy of the electron is the rest energy plus the energy lost by the photon, as indicated on the figure along the hypotenuse. In writing this expression for the total energy of the electron, we have used the law of conservation of energy. The momentum triangle in Fig. 5-3(b) of course represents conservation of momentum. We can now apply the cosine rule to both triangles to find expressions for p^2 and then equate the two expressions to eliminate p^2 . Before doing this, we divide all terms in Fig. 5-3(c) by c . The result is

$$\frac{h^2}{\lambda_0^2} + \frac{h^2}{\lambda_1^2} - 2 \frac{h}{\lambda_0} \frac{h}{\lambda_1} \cos \alpha = \left(m_e c + \frac{h}{\lambda_0} - \frac{h}{\lambda_1} \right)^2 - m_e^2 c^2. \quad (5-2)$$

After canceling the square terms and some rearrangement, we obtain

$$2 \frac{h^2}{\lambda_0 \lambda_1} (1 - \cos \alpha) = 2 m_e c \left(\frac{h}{\lambda_0} - \frac{h}{\lambda_1} \right).$$

After multiplication with $\lambda_0 \lambda_1 / 2 h m_e c$, we obtain

$$\lambda_1 = \lambda_0 + \frac{h}{m_e c} (1 - \cos \alpha). \quad (5-3)$$

The quantity $h/m_e c$ has the dimension of length. If we insert numerical values, we obtain

$$\lambda_c = \frac{h}{m_e c} = 0.02426 \text{ \AA}, \quad (5-4)$$

which is called the *Compton wavelength* of the electron.

Equation (5-3) shows that the wavelength shift should vary with scattering angle α as $1 - \cos \alpha$. This is in agreement with the data shown in Fig. 5-2. The magnitude of the shift is also as predicted, as can be seen most easily for $\alpha = 90^\circ$. The broadening of the modified or Compton peaks seen in Fig. 5-2 is a result of the motion of the electron in the atom. The theory above was based on an electron initially at rest. If the motion of the electron is taken into account, the broadening of the modified peak can be completely explained.

The appearance of the modified peak is therefore further evidence for the view that electromagnetic radiation consists of photons; that is, packets of electromagnetic energy. We now return briefly to the unmodified line. This also is possible to understand in terms of the photon concept. The unmodified line can be thought of as arising from scattering by electrons that are not torn loose from the atom; they remain in their initial state, and the whole atom takes up the recoil energy. Compton scattering, or the modified line, arises from events in which the electrons are knocked out of the atom and therefore absorb momentum and energy. This energy can only come from a reduction in the energy of the incident photon; that is, in an increase in the wavelength of the photon involved in the process. In the corpuscular theory, then, one line represents elastic scattering with the atom; the other represents inelastic scattering in which the atom is disrupted. However, all scattered photons do reveal their wave structure in the spectrometer by which they are analyzed.

It appears that electromagnetic radiation must be considered as a wave in some processes and as a particle in others. This does not occur randomly, however; the processes can be sorted into the two following types: Those that require the wave nature are ones which may be called propagation processes. An important part of their explanation is the consideration of the path or paths traveled by the light, as in interference experiments where a path difference is determined. The processes that require the particle nature may be called interaction processes. The radiation interacts with matter to produce a resultant absorption or scattering.

This dual nature of light was not readily accepted. The main reason for this is the apparently contradictory aspects of the two natures. A wave is specified by a frequency ν , wavelength λ , phase velocity u , amplitude A , and intensity I . These are not all independent. Thus the velocity, frequency, and wavelength are related by $u = \nu\lambda$. A wave is necessarily spread out and occupies a relatively large region of space. Actually, a sinusoidal wave would have to have infinite length to have a sharp frequency or wavelength. It can be

shown, theoretically or experimentally, by harmonic analysis to consist of a band spectrum. A particle, on the other hand, is specified by mass m , velocity v , momentum p , and energy E . The characteristic which seems in conflict with a wave is that a particle, for instance an electron, is very small and presumably occupies a definite position in space. It is difficult to accept the conflicting ideas that light is a wave that is spread out over space and also a particle that is at a "point" in space. This acceptance is necessary, however, to explain all the results of the experiments which can be performed with light. (We use the word "light" to include the entire electromagnetic spectrum.)

We do have connections between the wave and particle characteristics of light. As indicated in Chapter 3, Planck related the energy of the photon, E , and the frequency of the wave, ν , by

$$E = h\nu. \quad (5-5)$$

In the treatment of Compton scattering above, we have used

$$p = h/\lambda \quad (5-6)$$

between the momentum of the photon, p , and the wavelength of the wave, λ . In addition, the intensity of the wave is related to the rate at which photons pass through a unit area. Consequently, the particle characteristics of light can be found from the wave characteristics, even though the concepts of wave and particle appear to contradict each other. We shall attempt to resolve this contradiction in Section 5-6.

5-2 THE DE BROGLIE HYPOTHESIS

The dual nature of light, made necessary by experimental results, was extended by deBroglie in 1924. He felt that nature was symmetrical and the dual nature of light should be matched by a dual nature of matter. His argument was that if light can act like a wave sometimes and like a particle at other times, then things like electrons, which were considered particles, should also act like waves at times.

To specify the wave properties, deBroglie proposed that the relation between the momentum and the wavelength of a photon (Eq. 5-6) is a general one, applying to photons and material particles alike. He therefore postulated that to any moving object there is associated a wavelength.

$$\lambda = \frac{h}{mv}. \quad (5-7)$$

This is called the deBroglie wavelength. These proposed waves were not electromagnetic waves but were a new kind of wave, which were called matter waves or *pilot* waves. The word *pilot* implies that these waves pilot or guide the particle. When deBroglie published his hypothesis, it was not supported

by any experimental evidence. His only real argument was his intuitive feeling that nature must be symmetrical. He could make important deductions, however, from his postulate, the results of which were very suggestive, if not entirely convincing (see Sections 5-3 and 5-6).

At this point we may consider the fact that the wavelength is not sufficient to specify a wave completely. The frequency or velocity must also be known. We choose to define the frequency of the matter wave by extending the photon analogy, $\nu = E/h$, and by using the relativistic energy expression, $E = mc^2$. Since the phase velocity of any wave motion is $u = \nu\lambda$, we find the velocity of the waves associated with a particle to be $u = \nu\lambda = (E/h)(h/mv)$. Thus we have

$$u = \frac{mc^2}{h} \frac{h}{mv} = \frac{c^2}{v} \quad (5-8)$$

In this equation, v is the speed of the material particle, which must be *less* than the speed of light, c ; thus u is *greater* than the speed of light. The speed of the mass-energy of the particle does not exceed the speed of light in free space, but the phase velocity of its associated waves does. This result does not conflict with the concepts of relativity, since the speed of light is a limiting speed only for mass-energy. (See Appendix 3.) As it turns out, the deBroglie wavelength of a particle can be measured, but neither the frequency nor the phase velocity can.

5-3 BOHR'S FIRST POSTULATE

The theoretical implications of the deBroglie wavelength of matter are interesting. By making a very plausible assumption, we can relate this wavelength to the Bohr model of the atom.

A plucked guitar string will oscillate with transverse displacements in such a fashion that there will be a node at each end. Similarly, an acoustical resonator, an organ pipe, if closed at both ends and excited by a rapidly varying pressure through an inlet close to one end can resonate with displacement nodes at both ends. To get resonance, i.e., large displacements for only small driving pressures, the frequency of the driving pressure has to be chosen such that an integral number of wavelengths equals the length of the resonator.

If we bend the acoustical resonator into a circle, a doughnut, with no obstructing walls inside, resonance can be obtained for wavelengths satisfying the condition

$$2\pi r = n\lambda,$$

where r is the radius of the circle formed by the center line of the tube and n is an integer.

Let us now assume that the Bohr orbits correspond to standing electron

waves, analogous to the circular resonator. If we use the above condition with the deBroglie wavelength, we have

$$2\pi r = \frac{nh}{m_e v} \quad (5-9)$$

Recalling that the angular momentum of a particle moving in a circular orbit is $m_e v r$, we find that the angular momentum of the Bohr electron is

$$m_e v r = n \frac{h}{2\pi}, \quad (5-10)$$

which is precisely Bohr's first postulate. This discussion should not be interpreted as deriving Bohr's postulate, for essentially what we have done is replace Bohr's postulate with deBroglie's postulate, with the additional assumption that electrons in stationary states are represented by standing waves.

5-4 MATTER REFRACTION

Einstein pointed out that if the deBroglie hypothesis is valid, then it should be possible to diffract electrons. Schrödinger felt that if deBroglie were right, then the waves associated with matter should suffer refraction.

Light usually travels in straight lines, but when it goes from one medium to another it is refracted. Refractive bending is due to changes in the velocity of propagation of light, which is low in a medium of high refractive index. We are aware of abrupt refractions such as occur at the surfaces of a lens. However, the refractions at layers of air of differing temperatures are quite gradual. When the summer sun beats on a blacktop highway, the layers of air next to the road are expanded. Although the refractive index of air is very close to unity, the hot air over the highway has an index even nearer unity. Light coming down to the highway enters a region of lower index and is refracted away from the normal because of the refractive index gradient. If the light approaches this region of index gradient at a grazing angle, total reflection causes the familiar mirage effect. In this case, the bending of the path of light by refraction is not abrupt. The light rays form a continuous curve.

Schrödinger felt that the continuous curved paths of material objects might be such a continuous refraction of the associated matter waves. To see how this works out, we consider the following example. The parabolic flight of a baseball is a simple case of a material body moving in a curved path. At the top of the flight the path is concave downward, the instantaneous velocity v is horizontal, and the path may be regarded momentarily as the arc of a circle of radius of curvature R . The acceleration of the ball is the centripetal acceleration, v^2/R , which is the acceleration caused by gravity, g .

Equating these two expressions for the acceleration, we can solve for the radius of curvature of the path:

$$R = \frac{v^2}{g} \quad (5-11)$$

To express this result in terms of energy, we note that the total energy E of the baseball is constant and that the gravitational potential energy is $E_p = m_0gy$, where y is the height of the ball above the ground. The velocity of the ball is so small that we may use classical physics. Since the kinetic energy must be $(E - E_p)$, we have

$$E_k = \frac{1}{2}m_0v^2 = E - E_p$$

or

$$v^2 = \frac{2(E - E_p)}{m_0} \quad (5-12)$$

so that R , in terms of energy, becomes

$$R = \frac{2(E - E_p)}{m_0g} \quad (5-13)$$

Having found R by classical, nonrelativistic means, we next attempt to solve the same problem by considering the refraction of matter waves.

We apply Eq. (5-12) and $u = c^2/v$ to determine the phase velocity of the associated waves of the baseball, and obtain

$$u = c^2\sqrt{m_0/2(E - E_p)} = c^2\sqrt{m_0/2(E - m_0gy)}, \quad (5-14)$$

where $E_p = m_0gy$. It is evident that u is a function of the height y , and that u increases when y increases. This means that the higher the ball, the less is the "refractive index" of the space in which the associated waves move. Let us again compute the radius of curvature that this "refraction" imparts to the trajectory of the ball.

We assume, as before, that for an instant dt the ball moves on the arc of a circle of radius R . As in the study of optical refraction, we shall talk in terms of an infinitesimal wavefront of width dy perpendicular to the "ray". In Fig. 5-4 the phase waves move at a height y above the earth, and they curve concave downward because the top of the wavefront moves faster than the bottom. From the figure we find that

$$d\theta = \frac{u dt}{R} = \frac{(u + du) dt}{R + dy},$$

yielding

$$R = \frac{u}{du/dy} \quad (5-15)$$

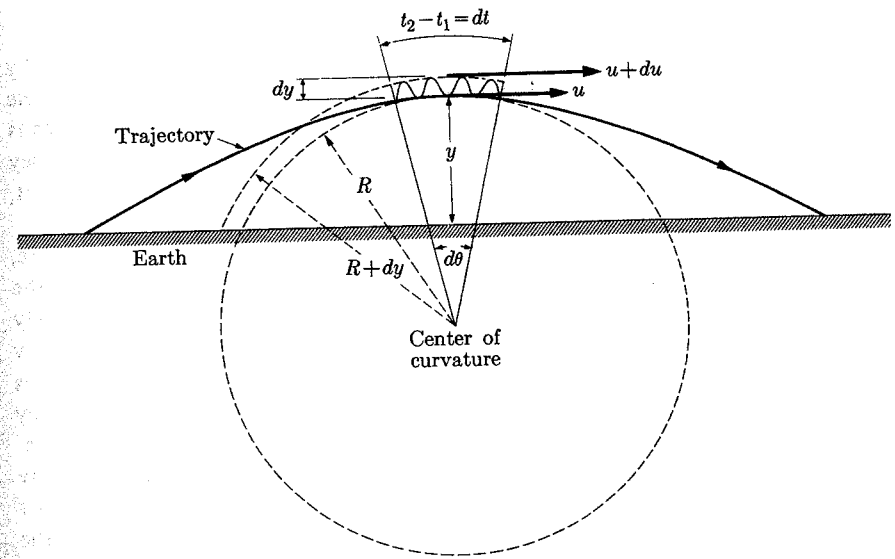


Fig. 5-4 Wave-mechanical representation of projectile motion.

To find du , we first put Eq. (5-14) in the form

$$u(E - m_0gy)^{1/2} = c^2 \left(\frac{m_0}{2} \right)^{1/2}$$

and then differentiate u with respect to y . The result reduces to

$$du = \frac{1}{2} \frac{m_0g}{E - m_0gy} u dy \quad (5-16)$$

Substituting this expression for du in Eq. (5-15), we get a relation which simplifies to

$$R = \frac{2(E - E_p)}{m_0g} \quad (5-17)$$

Agreement between Eqs. (5-13) and (5-17) supports Schrödinger's idea that it may be possible to devise a system of mechanics in which the paths of rays of matter waves replace the classical Newtonian trajectories. His great success in this respect is described in the next chapter.

Thus far we have presented no real experimental evidence, such as the observation of interference effects, that could provide convincing proof of the wave nature of light. However, in 1925 Elsasser deduced from deBroglie's theory that a beam of electrons diffracted by a crystal should show interference phenomena. This prediction eventually led to the experimental verification of the wave nature of matter.

5-5 THE DAVISSON AND GERMER EXPERIMENT

In 1927 Davisson and Germer* were studying the scattering of electrons by nickel. Their technique was reminiscent of both Rutherford alpha-particle scattering and Compton x-ray scattering. They directed a beam of electrons onto a block of nickel and measured the intensity of the electrons as they scattered from the nickel in different directions. In the course of the experiment, their vacuum system broke accidentally and had to be repaired.

When the vacuum system broke the nickel target was at a high temperature, and the air caused the nickel to acquire a heavy coat of oxide. To remove the oxide from the block of nickel, Davisson and Germer reduced the oxide slowly in a high-temperature oven. When their apparatus was reassembled, they began to get very different results. Whereas the number of scattered electrons had previously become continuously less as the scattering angle increased, they now found that the number of electrons went through maxima and minima. *The electrons were being diffracted.* Using the familiar techniques of x-ray diffraction by crystals, Davisson and Germer computed the wavelength their electrons must have, and they found that this wavelength agreed with the deBroglie formula.

The prolonged heating to clean the nickel block had caused it to become a single crystal, and the electron diffraction pattern was completely analogous to x-ray diffraction by the Bragg technique (see Chapter 10). This experiment verified the deBroglie hypothesis and indicated that material particles have wave properties.

To consider the Davisson and Germer experiment in more detail, we show their apparatus schematically in Fig. 5-5. At the right is an electron gun that provides a collimated beam of electrons whose energy is known from the accelerating potential. These electrons were scattered by the nickel target, which could be rotated about an axis perpendicular to the page. The movable electron collector could be swung about the same axis as the target, so that it

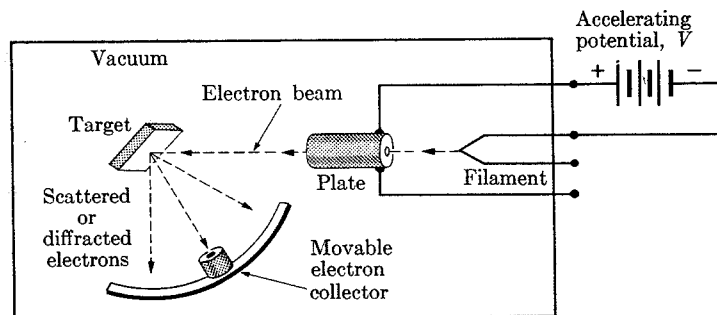


Fig. 5-5 Schematic diagram of the Davisson-Germer electron diffraction apparatus.

* C. P. Davisson and L. H. Germer, *Phys. Rev.* 30 (1927), p. 705.

could receive the electrons coming from the target in any direction included in the plane of the diagram. Figure 5-6 shows the results obtained for two target orientations both before and after the target was heat-treated. Since Davisson and Germer used 75-eV electrons, they could obtain the electron velocity from the classical expression

$$E_k = Ve = \frac{m_e v^2}{2}, \quad (5-18)$$

and substitute into the deBroglie relation, obtaining

$$\lambda = \frac{h}{m_e v} = \frac{h}{\sqrt{2Vem_e}}. \quad (5-19)$$

By inserting $V = 75$ V and the values of the other constants, we obtain $\lambda = 1.42$ Å. The distance between rows of atoms causing the diffraction in the nickel crystal was just a little larger, making the crystal an ideal grating for this kind of experiment. A quantitative check of the diffraction pattern showed that deBroglie's postulate is correct.

The deBroglie hypothesis was further verified in Germany when Estermann and Stern diffracted helium atoms from a lithium fluoride crystal, and in the United States when Johnson diffracted hydrogen from the same kind of crystal. G. P. Thomson, son of J. J. Thomson, obtained excellent powder diffraction patterns (see Chapter 10) by sending a collimated beam of electrons through very thin sheets of various metals. Figure 5-7(a) shows an electron diffraction pattern of aluminum. For comparison an x-ray diffraction pattern of aluminum is shown in part (b) of the figure. The effective wavelengths for the two patterns

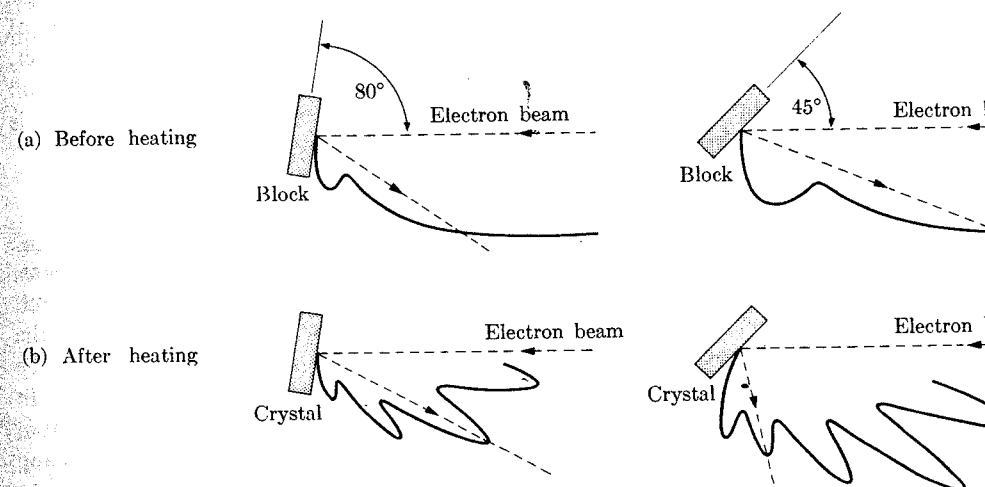


Fig. 5-6 (a) Electron scattering from a block of nickel, and (b) electron diffraction from a crystal of nickel.

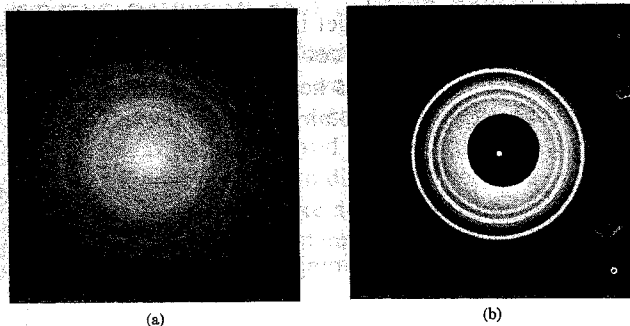


Fig. 5-7 (a) Electron diffraction pattern of aluminum, using electrons accelerated through 8000 volts. (b) X-ray diffraction pattern of aluminum, using K -radiation from copper. The wavelengths and geometry are different for the two photographs. A lead disk was placed over the center of the x-ray film for most of the exposure.

are different but the similarities are evident. Davisson and Germer, using electrons instead of x-rays, repeated an experiment earlier carried out by A. H. Compton on diffracting soft x-rays from a man-made grating at grazing incidence.

With the complete verification of the deBroglie hypothesis, we have arrived at a point where our atomic world has strange aspects. Compton scattering showed that waves have particle aspects and the deBroglie hypothesis shows that particles have wave characteristics.

In the following two sections we shall discuss the mathematical theory of wave groups and in the rest of the chapter some of the physical implications. We are now deviating from a description of the historical development of modern physics and going into a more formal development of wave mechanics. In Section 5-6 we shall attempt to resolve this duality more seriously than Eddington did when he humorously suggested that the primordial entity is really a "wavicle."

5-6 WAVE GROUPS

Although the interference effects compel us to accept the fact that, like light, material particles have the dual nature of waves and particles, it is still difficult to see how the wave extended over a region of space does not conflict with the small particle located at a specific position. This apparent conflict can be resolved by the formation of what is called a wave group or wave packet. In essence this is a wave which extends over a very limited region of space. It is formed by applying the principle of superposition to many waves. When many waves travel through the same medium, the resultant wave is the summation (in our case it will be algebraic) of all the waves. In acoustics such a summation of two waves of slightly different frequencies produces beats, which are

fluctuations in the amplitude of the resultant wave. We shall see that when more and more frequencies are added, the regions where the amplitude is large can be made smaller.

To simplify the discussion of the superposition we will use a one-dimensional wave; that is, a wave whose displacement, y , depends on the position along a line, x , and the time, t . A sinusoidal wave with amplitude A may be written as

$$y = A \sin 2\pi \left(\frac{x}{\lambda} - vt \right) = A \sin (kx - \omega t), \quad (5-20)$$

where we have introduced k , the propagation number which equals $2\pi/\lambda$, and the angular frequency $\omega = 2\pi\nu$. Even with one-dimensional conditions it is difficult to draw the wave, since there are two independent variables. What we usually do is hold one fixed and vary the other. Thus we either draw the displacement as a function of position at some fixed time (equivalent to a snapshot) or the displacement as a function of time at some fixed position. In the following development, we will use time as the variable. The results would be the same using the position as the variable if t were replaced by x and ω were replaced by k .

The time dependence of a sinusoidal wave with amplitude A can be considered as a component of a vector of length A which is rotating with a constant angular velocity ω , as shown in Fig. 5-8(a). Such a rotating vector is called a *phasor*. Since the sum of the components of many vectors is the component of the vector sum, we can get the time dependence of the sum of many waves by adding many phasors. Let us add n waves with angular velocities between ω_1 and ω_n . To simplify the addition we choose waves with the same amplitude and angular velocities which vary uniformly, so that $\omega_2 - \omega_1 = \omega_3 - \omega_2 = \dots = \omega_n - \omega_{n-1} = \delta\omega$. Since there are $n - 1$ intervals between ω_1 and ω_n , this interval is

$$\delta\omega = \frac{\omega_n - \omega_1}{n - 1}.$$

If all the phasors are parallel at $t = 0$, they will be spread out uniformly at time t , as indicated in Fig. 5-8(b). The angle between adjacent phasors will be given by

$$\delta\theta = (\delta\omega)t = \left(\frac{\omega_n - \omega_1}{n - 1} \right) t. \quad (5-21)$$

The magnitude of the vector sum is the amplitude of the resulting wave, while the projection of the resultant on the vertical axis is the instantaneous displacement. We assume that $\delta\omega$ is so small that the amplitude does not change very much during one revolution. The amplitude represents the envelope of the oscillations and we will determine the general shape of this envelope. As

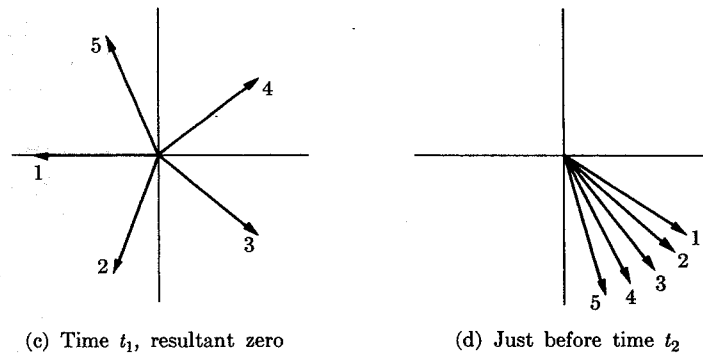
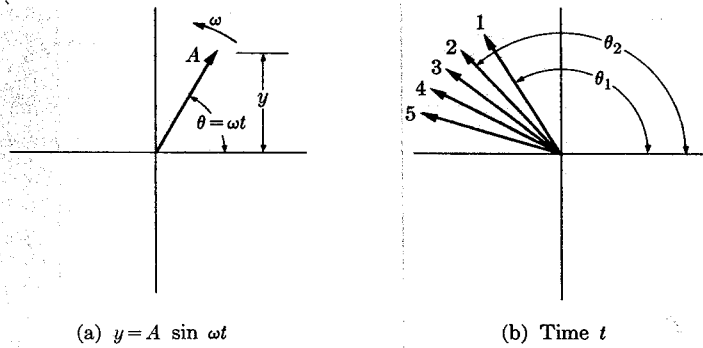


Fig. 5-8 (a) Single phasor. (b) Five phasors a short time after $t = 0$. (c) Five phasors with zero resultant. (d) Five phasors a short time before they become parallel.

the phasors fan out from $t = 0$, the magnitude of the resultant decreases to zero. This first zero occurs when the fan covers the entire angle 2π and the angle between adjacent phasors is $2\pi/n$, as shown in Fig. 5-8(c) for five phasors. If we call the time for the first zero t_1 , Eq. (5-21) becomes

$$\frac{2\pi}{n} = \left(\frac{\omega_n - \omega_1}{n - 1} \right) t_1,$$

which can be solved for t_1 to give

$$t_1 = \left(\frac{2\pi}{\omega_n - \omega_1} \right) \frac{(n - 1)}{n}. \quad (5-22)$$

For a while after t_1 the magnitude of the resultant will be small, since the phasors will still be spread out. Eventually, however, the second phasor will catch up to the first and at this time all the other phasors will also be aligned with the

first. The resultant will be the same magnitude that it was when $t = 0$. Fig. 5-8(d) shows the phasors just before this occurs. If we call the time when they are aligned t_2 , the angle between adjacent phasors is 2π and Eq. (5-21) becomes

$$2\pi = \left(\frac{\omega_n - \omega_1}{n - 1} \right) t_2,$$

which gives for t_2 :

$$t_2 = \left(\frac{2\pi}{\omega_n - \omega_1} \right) (n - 1). \quad (5-23)$$

After time t_2 has elapsed, the envelope will repeat the shape it took between $t = 0$ and $t = t_2$, so that we have the magnitude of the sum of the phasors as a function of time.

The quantitative variation of the envelope of the resulting wave will depend on the number of waves added together; however, the preceding qualitative discussion gives us some idea of how the resultant wave will appear. This is shown in Fig. 5-9(a). The wave has a large amplitude only in limited regions with sections of relatively low amplitude between. The regions of large amplitude are called the *wave groups* and the individual waves which are added together are called the *phase waves*. Remember that we chose to consider time as the variable. If we had varied x at a fixed time, the analysis would have been the same with ω replaced by k . The resultant wave as a function of position is shown in Fig. 5-9(b).

Although we have managed to produce wave groups, there are too many of them to reasonably represent a particle. For the wave to appear like a particle there should be only one group. This can be accomplished if we can get the time between the group maxima, t_2 , to be infinite. A consideration of Eq. (5-23) shows that this can be done by having n become infinite. A *single* wave group can be formed by the addition of an infinite number of waves. Note that this does not mean that the frequency difference in the denominator of Eq. (5-23) must be infinite. An infinite number of frequencies can be contained in a finite frequency interval. The "size" of the group in time is $2t_1$, which we call the *time duration* of the group. For an infinite number of waves Eq. (5-22) for t_1 becomes

$$t_1(n = \infty) = \frac{2\pi}{\omega_n - \omega_1}.$$

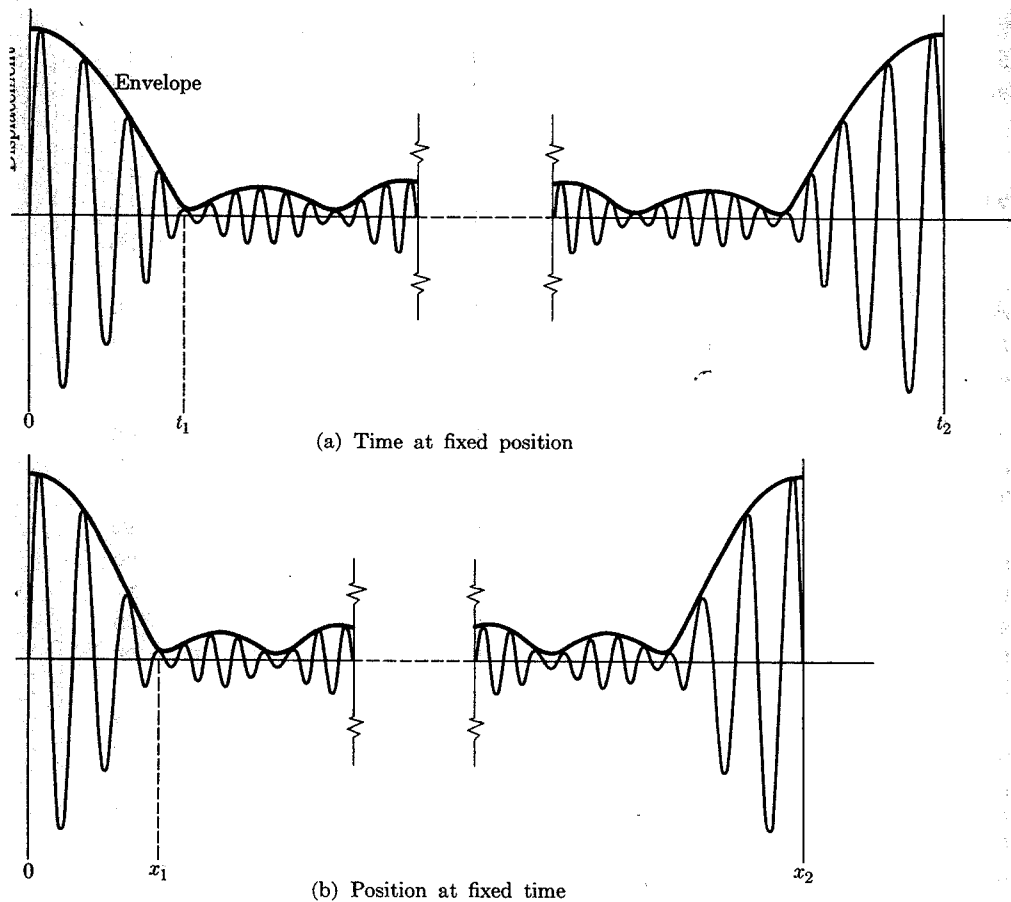
If we call $\omega_n - \omega_1$ the frequency spread $\Delta\omega$, we have

$$2t_1 = \Delta t = 4\pi/\Delta\omega; \quad (5-24)$$

the time duration of the wave group is determined by the frequency spread. In the same way the spatial size of the group, Δx , is given by

$$\Delta x = 4\pi/\Delta k; \quad (5-25)$$

the spread of propagation numbers determines the size of the group.



9-9 A resultant wave produced by summation of many waves with different frequencies; (a) as a function of time, (b) as a function of position.

Although we have been able to construct a wave group which has the particle-like characteristic of extending over a very limited region of space, there is still the question of the propagation velocity of the group. Each of the phase waves has a phase velocity $u = v\lambda = \omega/k$. In a nondispersive medium all the phase waves have the same velocity and consequently the group will move with this velocity. In a dispersive medium the phase velocities differ and the question of the group velocity is more complicated.

Let us consider two of the phase waves, which can be written as

$$y_1 = A \cos(k_1 x - \omega_1 t)$$

and

$$y_2 = A \cos(k_2 x - \omega_2 t),$$

for which the phase velocities are $u_1 = \omega_1/k_1$ and $u_2 = \omega_2/k_2$. The functions have been chosen such that the two waves are in phase and maximum at $x = 0$ and $t = 0$. The addition of these two waves can be done by using the trigonometric identity

$$\cos a + \cos b = 2 \cos \frac{1}{2}(a - b) \cos \frac{1}{2}(a + b).$$

The resultant wave becomes

$$\begin{aligned} y &= y_1 + y_2 \\ &= 2A \cos \frac{1}{2}[(k_2 - k_1)x - (\omega_2 - \omega_1)t] \cos \frac{1}{2}[(k_1 + k_2)x - (\omega_1 + \omega_2)t]. \end{aligned}$$

If the propagation numbers and frequencies differ only by differential amounts, we have

$$\begin{aligned} k_2 - k_1 &= dk, & \omega_2 - \omega_1 &= d\omega, \\ \frac{1}{2}(k_1 + k_2) &\approx k_1 & \text{and} & \quad \frac{1}{2}(\omega_1 + \omega_2) \approx \omega_1. \end{aligned}$$

The resultant wave is then

$$y = 2A \cos \frac{1}{2}[dk x - d\omega t] \cos(k_1 x - \omega_1 t). \quad (5-26)$$

The second cosine function times A is one of the original waves. The cosine function in front modulates this wave with another cosine function of wavelength π/dk and a frequency $(d\omega/\pi)$. From the product of these we can get the velocity of propagation of the modulation, which is the group velocity v_g :

$$v_g = \left(\frac{\pi}{dk}\right) \left(\frac{d\omega}{\pi}\right) = \frac{d\omega}{dk}. \quad (5-27)$$

The group velocity depends on the way in which the frequency varies with the propagation number. Since we have considered only two phase waves, it is possible that v_g will differ for different pairs of phase waves; that is, the group velocity may be a function of frequency. When many waves are added, the derivative of Eq. (5-27) is evaluated for the central frequency of those used in the summation.

If the wave group is to represent a particle, then it is necessary that the speed of the group and the speed of the particle be the same. If these speeds differed, the particle would soon be in a region where the amplitude of the wave is negligible and the wave would not give a useful indication of the position of the particle. Using the mass-energy relation from relativity, we can find the particle velocity in terms of its momentum and energy:

$$v = p/m = pc^2/mc^2 = pc^2/E. \quad (5-28)$$

To get the group velocity in the same terms we use $p = h/\lambda$ and $E = hv$ which are written as

$$k = \frac{2\pi p}{h} \quad \text{and} \quad \omega = \frac{2\pi E}{h}. \quad (5-29)$$

The group velocity can then be written as

$$v_g = \frac{d\omega}{dk} = \frac{dE}{dp}. \quad (5-30)$$

To evaluate this we need the energy-momentum relationship from relativity, Eq. (A3-48);

$$E^2 = p^2 c^2 + m_0^2 c^4.$$

Differentiating this, we obtain

$$2E dE = 2pc^2 dp.$$

The group velocity becomes

$$v_g = \frac{dE}{dp} = \frac{pc^2}{E}. \quad (5-31)$$

The particle velocity (Eq. 5-28) thus equals the group velocity (Eq. 5-31). We therefore see that the choices that were made for the frequency and wavelength to be associated with the particle also lead to the satisfying result that the wave group and the particle have the same speed.* Thus it is possible to have a wave motion which has the particle characteristic of being in a small region of space and which will move with the particle's speed.

5-7 FOURIER ANALYSIS; ORTHOGONALITY

Most readers will be familiar with the mathematics of Fourier series used to describe periodic functions. For instance, a function of x with a period L can be expanded in a Fourier series as follows:

$$f(x) = \sum_{n=0}^{\infty} \left(A_n \cos \frac{2\pi nx}{L} + B_n \sin \frac{2\pi nx}{L} \right). \quad (5-32)$$

For example, the transverse displacement of the plucked guitar string mentioned in Section 5-3 can be described by this function. We then think of the guitar string as continuing indefinitely, and the simplest description is obtained by making the period L equal to twice the length of the string. Thus the length of the string is half the wavelength of the *fundamental* (lowest frequency) for which $n = 1$. We further have $A_n = 0$ for all values of n because the cosine functions do not satisfy the boundary requirement that the displacement is zero for $x = 0$ and $x = L$. Therefore B_1 is the amplitude of the fundamental, B_2 is the amplitude of the second harmonic, B_3 is the amplitude of the third harmonic, etc.

* It is a curious fact that if we had used the classical expression $E = E_k = \frac{1}{2}mv^2 = p^2/2m$, we would also have found agreement between group and particle velocities.

Equation (5-32) can be written as

$$f(x) = \sum_{n=-\infty}^{n=\infty} C_n e^{i2\pi nx/L}. \quad (5-33)$$

The proof of this statement is left to one of the problems. Note that the integer n now runs from $-\infty$ to $+\infty$. We thereby get positive and negative exponentials under the summation sign as needed to produce cosine and sine functions. Assuming that the coefficients A_n and B_n in Eq. (5-32) are real, as required for instance in the case of a plucked string, the coefficient C_n will be complex.

In order to find the coefficients C_n , we assume that the function $f(x)$ is given, for instance, in tabular form or in analytic forms broken up over several parts of the period. Examples of the latter are sawtooth functions and square waves well known in electronics. If $f(x)$ is known in such a form that it can be integrated, we find the coefficients C_n in the following way. We multiply each side of Eq. (5-33) with $e^{-i2\pi mx/L}$ and integrate over x from $-L/2$ to $+L/2$:

$$\int_{-L/2}^{L/2} f(x) e^{-i2\pi mx/L} dx = \sum_{n=-\infty}^{\infty} C_n \int_{-L/2}^{L/2} e^{i2\pi(n-m)x/L} dx. \quad (5-34)$$

The function in the integrand on the right-hand side of Eq. (5-34) is a sum of a sine function and a cosine function, both with periods equal to $L/(n-m)$, except when $n = m$, in which case the function is unity. For $n \neq m$, the integrals from $-L/2$ to $+L/2$ are integrals over a whole number of wavelengths, and they therefore vanish. We can then write

$$C_m = \frac{1}{L} \int_{-L/2}^{L/2} f(x) e^{-i2\pi mx/L} dx. \quad (5-35)$$

We have here transposed the two sides of Eq. (5-34) and written C_m instead of C_n , because only the term in the series for which $n = m$ remains on the right-hand side of Eq. (5-34).

Equation (5-33) can be used to describe any periodic function with period of length L and with the coefficients C determined by the aid of Eq. (5-35). For instance, this analysis can be used to describe the transverse displacements of a plucked guitar string, as described above, because the function is defined over a limited range in x and we can therefore arbitrarily call this range half the period. The function (5-33) can also be used, for instance, to describe the pressure oscillation in air near a piano in which middle C has been struck. The independent variable x is then time, and L is the period. The coefficients

C will be slowly decaying functions of time with a different decay rate for the various harmonics.*

The functions $e^{i2\pi nx/L}$, with n being an integer running from $n = -\infty$ to $n = +\infty$, are *orthogonal* functions in the interval $x = -L/2$ to $x = +L/2$. Two functions $\phi_n(x)$ and $\phi_m(x)$ are orthogonal in the interval $x = a$ to $x = b$ if

$$\int_a^b \phi_m^* \phi_n dx = 0, \quad \text{for } n \neq m. \quad (5-36)$$

Here ϕ_m^* is the complex conjugate of ϕ_m , that is, ϕ_m^* is produced by changing the sign of all terms containing $i = \sqrt{-1}$.

The orthogonality of the functions used in Fourier analysis is, of course, necessary for Eq. (5-34) to reduce to Eq. (5-35). It is not only sine and cosine functions and complex exponentials that form orthogonal sets of functions. In later chapters we shall discuss further the fact that the solutions of Schrödinger's wave equation in general form orthogonal sets, and that arbitrary functions can be expanded in terms of these functions in a similar manner as that expressed by Eq. (5-32) or (5-33).

Another feature of the trigonometric functions or complex exponentials is that they form a *complete* set. This means that an infinite series, such as Eq. (5-33), can always be found to describe $f(x)$ exactly, provided $f(x)$ is finite and has a limited number of discontinuities in the interval $x = -L/2$ to $x = +L/2$. For the proof of this statement, we have to refer to a textbook in mathematics.

In the discussion above, we have defined the function $f(x)$ in an interval $-L/2$ to $+L/2$, and it is clear from the formula that the function will repeat itself in successive intervals of length L . Now we see that we can increase the length L of the interval to include any region that we may be interested in, and it would not matter if $f(x)$ repeated itself outside these limits. Indeed, there is no reason why we should not let L go to infinity. In order to do so, we first write Eq. (5-33) as

$$f(x) = \sum_{n=-\infty}^{n=\infty} \frac{LC_n}{2\pi} e^{ikx} \Delta k, \quad (5-37)$$

where we have introduced a new variable

$$k = 2\pi n/L, \quad (5-38)$$

* We are oversimplifying a bit. The middle C key strikes not one but three strings in the piano. The three strings are intentionally tuned to slightly different resonance frequencies (fundamentals): otherwise, the piano would sound dull. Also, the "harmonics" do not have exactly two or three times the frequency of the fundamental because of stiffness of the strings.

which we recognize as being the propagation number $k = 2\pi/\lambda$. We further obtain $\Delta k = 2\pi\Delta n/L$ with $\Delta n = 1$.

For an expression such as Eq. (5-33) to be meaningful, the series must converge. This means that the coefficients C_n , in general, will decrease as n increases. However, one can get an arbitrarily good description of $f(x)$ with a truncated series, that is, with a finite number of terms. The longer the interval L , the more terms are needed, and each individual C_n will then be smaller. Coming back to Eq. (5-37), we see that for $f(x)$ to remain finite, the product of L and C_n must remain finite, so C_n approaches zero as L goes to infinity. We therefore introduce a new function to replace the product LC_n :

$$g(k) = (2\pi)^{-1/2} LC_n. \quad (5-39)$$

The factor $(2\pi)^{-1/2}$ is included for symmetry reasons, as will be immediately evident. Making this substitution in Eq. (5-37) and converting the sum to integrals, we obtain

$$f(x) = (2\pi)^{-1/2} \int_{-\infty}^{\infty} g(k) e^{ikx} dk. \quad (5-40)$$

This is a Fourier series, in which the wavelength does not change in discrete jumps as in Eq. (5-33) or (5-32) but rather varies continuously (or stated differently, the wavelength changes by infinitesimal steps). The amplitude function $g(k)$ is found very simply by substituting Eq. (5-39) into Eq. (5-35), changing the subscript from m to n . The result is

$$g(k) = (2\pi)^{-1/2} \int_{-\infty}^{\infty} f(x) e^{-ikx} dx. \quad (5-41)$$

The function $g(k)$ is called the Fourier transform of $f(x)$, and the two functions $f(x)$ and $g(k)$ are called Fourier inverse functions.

As an example, consider the Gaussian distribution function

$$f(x) = \pi^{-1/4} \sigma^{-1/2} e^{-x^2/2\sigma^2}, \quad (5-42)$$

where σ is the standard deviation or root-mean-square deviation from the mean value $\bar{x} = 0$. This function is plotted in Fig. 5-10. We find the Fourier transform from Eq. (5-41) to be

$$\begin{aligned} g(k) &= 2^{-1/2} \pi^{-3/4} \sigma^{-1/2} \int_{-\infty}^{\infty} e^{-x^2/2\sigma^2} e^{-ikx} dx \\ &= 2^{1/2} \pi^{-3/4} \sigma^{-1/2} \int_0^{\infty} e^{-x^2/2\sigma^2} \cos kx dx. \end{aligned} \quad (5-43)$$

We have here written $e^{-ikx} = \cos kx - i \sin kx$ and made use of the fact that an antisymmetric function (i.e., the one containing $\sin kx$) integrates out to

zero. The last integral can be found in a table of definite integrals*. Inserted into Eq. (5-43), it gives

$$g(k) = \pi^{-1/4} \sigma^{1/2} e^{-k^2 \sigma^2 / 2}. \quad (5-44)$$

This transform is also plotted in Fig. 5-10.

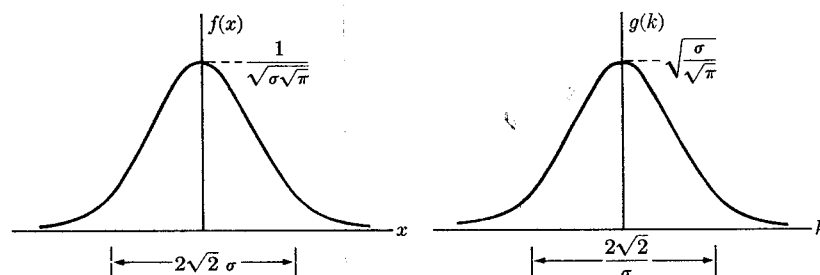


Fig. 5-10 The Gaussian function $f(x)$ and its Fourier transform $g(k)$ which is also Gaussian.

We can write the exponential in Eq. (5-44) as $e^{-k^2/2\sigma_k^2}$. The standard deviation σ_k for the transform can be found by comparing Eqs. (5-42) and (5-44). We find that

$$\sigma_k = 1/\sigma. \quad (5-45)$$

Consider the Gaussian (Eq. 5-42) as an example of a deBroglie pilot wave. The transform (Eq. 5-44) then represents the spectrum of propagation numbers k necessary to describe this wave or the wavelength spectrum with $\lambda = 2\pi/k$. If we use the standard deviations as measures of the width of the wave train and its transform, we find from Eq. (5-45) that

$$\Delta x \Delta k \approx 1. \quad (5-46)$$

Using the widths $2\sqrt{2}\sigma$ and $2\sqrt{2}/\sigma$ indicated under the curves in Fig. 5-10, we obtain

$$\Delta x \Delta k = 8, \quad (5-47)$$

which can be compared with Eq. (5-25).

5-8 WAVE-PARTICLE DUALITY

The wave-group idea is an attempt to resolve the conflict contained in the fact that some explanations of experiments require the use of waves while others require the use of particles. This interpretation means that an electron is a group of matter waves and a photon is a group of electromagnetic waves,

that is, there are only waves in nature but they form wave packets which we call particles. As indicated in Section 5-4, the trajectories of the particles are due to the refractions of the waves. Macroscopic objects consist of many of these wave groups and the interactions between objects are simply interactions of waves.

Although this "reality" of the waves seems reasonable, there are some difficulties associated with it. When a wave is incident on a boundary between two media, it generally splits into a reflected wave and a refracted wave. The incident wave group becomes two groups. If the wave group is to be an electron, where the boundary would be produced by a change in electric potential energy, we know that the electron does not split. It is difficult to see how the two wave groups, one reflected and one refracted, can be the single electron. In addition, the Coulomb force, which is stated for point charges and acts between electrons, cannot be handled conveniently with this interpretation.

Another possible interpretation was presented by deBroglie. In this the particles are "real" and the associated waves are pilot waves which guide the particle and are to be looked upon as probability waves. The amplitude of these probability waves at a certain position is a measure of the probability of the particle being at that position. The pilot waves are abstract quantities and the word "wave" is used as it is, for instance, in the phrases "wave of enthusiasm" and "crime wave." Since the waves are not directly observable, there is no necessity for a medium. This interpretation removes the difficulty of the wave group concept when the wave is partially reflected and partially refracted. For the probability waves, the amplitude of the reflected wave determines the probability that the particle reflects from the boundary and the amplitude of the refracted wave determines the probability that the particle penetrates the boundary. A single particle will do *only* one or the other, but a large number of particles will divide according to the probabilities.

This pilot wave interpretation, which means that a light beam is a stream of photons, also runs into difficulty. Suppose that we pass a light beam through a pair of slits separated by a small distance, as in the interference experiments of Young. The interference pattern produced on a screen consists of alternate light and dark bands. The positions of these bands are determined by the differences of the paths of the two waves proceeding from the slits to the screen. The alternate light and dark bands represent alternate large and small probabilities of a photon arriving at the respective positions on the screen. If one of the slits is covered, the interference pattern changes, which means the probabilities of where the photon will arrive at the screen changes. For example, the photon may now have a large probability of arriving at a position where the previous probability was very small. If the photons are real, however, they *must* go through one slit or the other. Consequently, as the photon goes through one slit, its motion is influenced by the other slit and the photon is able to know whether the slit through which it did not pass is open or not.

* For instance, in *Handbook of Chemistry and Physics*, Chemical Rubber Publishing Company, Cleveland (any year).

This gives some "intelligence" to the particles which does not seem reasonable. We will return to this problem in Section 5-10.

The resolution of the conflict between waves and particles lies in an appraisal of what we mean by a wave and a particle. Both of these terms, when applied to the fundamental entities, are abstractions of the human mind which are arrived at by extrapolation from the macroscopic world of grains of sand and waves on strings. The following is another very clever and useful trick of the human mind. A hollow rubber ball has its center of gravity at its center. Discussion of most, but not all, of the motion of the ball can be greatly facilitated by regarding the ball as a point mass with all its mass at the center of gravity. The center of gravity has no objective reality, and if someone cuts the ball open, points to the center and says, "Ha! You see, there is no mass there," we reply that the center of gravity makes a poor description of what is at the center of the ball, but that it continues to be useful in describing the motion of the ball. No one description of the ball can ever completely represent what the reality of the ball is. In the same way the particle description and the wave description are each incomplete in attempting to describe physical reality.

The mistake of those who say that interference shows that light *is* a wave phenomenon is a verbal mistake that is made every day. We point to a map and say this *is* the United States. What we mean is that this diagram on a piece of paper is a scale representation of many of the physical and political features of the United States. We know that the real United States cannot be folded, rolled up, or burned. We know that the states are not different in color, only a few square inches in area, and completely flat. The map is a clever, useful, elegant model invented by the human mind. More may be learned about some aspects of the United States in one hour of map study than in a lifetime of looking at the real United States. We do not scoff at maps because they are unreal, we admire them as useful descriptions.

Both the wave and the particle are models we have constructed in attempting to describe matter. Quite naturally, we do not expect either model to give a complete description. Some properties, such as interference, are contained in one model, the wave, while other properties, such as mass, are contained in the other model, the particle. The two models complement each other in that together they give a description of matter. Thus we should say that the electrons are waves *and* particles, not waves *or* particles. The same statement can be made about electromagnetic radiation. During an experiment the particular model which is used is determined by the apparatus used.

Even though we admit that waves and particles are not "real," it is very awkward to talk about experimental procedures and results in such a way as to indicate this. Consequently, we will still make statements which seem to imply that particles exist; for example, we say that the intensity of the wave is a measure of the probability of the location of the particle. This is for con-

venience only. Both the wave and the particle are incomplete models and both are necessary for a description of all the properties of matter which are experimentally determined. With this interpretation, there is no conflict in the dual nature of matter or electromagnetic radiation.

5-9 THE HEISENBERG UNCERTAINTY PRINCIPLE

An important consequence of the wave-particle duality can be developed from the wave group analysis of Sections 5-6 and 5-7. In an attempt to get a wave that had a limited extent, we added many waves to form a wave group. If we correlate the wave model to the particle model by assuming that the amplitude of the group measures the probability of the particle being at that position, we see that there is still no certainty in knowing the location of the particle. It could be anywhere in the group.

To decrease the uncertainty in location of the particle, we have to reduce the size of the group, Δx . If we rearrange Eq. (5-25) into

$$\Delta x \Delta k = 4\pi, \quad (5-48)$$

the size of the group can be reduced by increasing the spread of propagation numbers, Δk . It appears that we may eliminate the uncertainty in position of the particle by using an infinite spread of propagation numbers. We see from $k = 2\pi p/h$ that the momentum of the particle is determined by the propagation number of the wave. If we use an infinite spread of propagation numbers, we will have an infinite spread in the momentum of the particle. When we decrease the uncertainty of the particle's position, we increase the uncertainty of the particle's momentum. If we put Eq. (5-48) in terms of momentum, we have

$$\Delta x \Delta p = 2h.$$

The coefficient of h in this expression was obtained through our simplification of using waves with the same amplitudes and with a uniform spread of frequencies. A different choice of these would give a different number for this coefficient. If we choose to characterize the uncertainties Δx and Δp by root-mean-square deviations rather than the widths of the central maximum as in Fig. 5-9, we find

$$\Delta x \Delta p_x \simeq \hbar. \quad (5-49)$$

Compare Eq. (5-46) with Eq. (5-49).

The subscript is added to the momentum to indicate that it is the momentum associated with the x -displacement. Equation (5-49) is interpreted as indicating that the uncertainty in position of the particle times the uncertainty in the associated momentum is approximately \hbar . The words *associated momentum* are used because in the three-dimensional case there are also momentum components in the y - and z -directions and with the x -position we use the

x-component of momentum. There are equivalent equations for the other directions:

$$\Delta y \Delta p_y \simeq \hbar, \quad (5-50)$$

$$\Delta z \Delta p_z \simeq \hbar. \quad (5-51)$$

These uncertainties are involved with the nature of matter and are not the same as the uncertainties introduced by the limited precision of some measuring device. In a practical experiment the uncertainties introduced by the equipment will usually be much larger than the ones associated with the wave-particle duality.

We can perform the same analysis with Eq. (5-24), $\Delta t = 4\pi/\Delta\omega$, where the frequency spread determined the time duration of the group as it passed a given position. Using $E = h\nu = h\omega/2\pi$, we obtain $\Delta t \Delta E \simeq \hbar$, or when using root-mean-square deviations,

$$\Delta t \Delta E \simeq \hbar. \quad (5-52)$$

This relationship can be interpreted as meaning that the uncertainty of the energy of the particle is dependent on the time interval used for measuring the energy.

This result throws light on a question not considered in the Bohr theory of atomic energy states. The excited states have finite lifetimes Δt and therefore an associated energy uncertainty, $\Delta E \approx \hbar/\Delta t$. Spectral lines emitted from a short-lived state are broader than lines emitted from long-lived states, and the widths can actually be observed with precision instruments.

The equations concerning uncertainties, that is, Eqs. (5-49) to (5-51), (5-31) and (5-32) are variant statements of the *Heisenberg Uncertainty Principle*. We look upon these statements as indicative of the inherent nature of the physical world. Thus it is impossible for us to know an exact position and an exact momentum of a photon or an electron. A precise knowledge of one can be obtained only at the expense of the precision of the other. Frequently, the uncertainty principle is introduced as being due to the act of measurement. For example, when the position of an electron is determined, the measurement introduces the uncertainty in position and momentum because of an interaction between the apparatus and the electron. This implies that the electron had an exact position and momentum before the measurement. We prefer the interpretation that the uncertainties are inherent in the nature of the things we do experiments with. Admittedly, this choice cannot be made on the basis of any physical result. Physics deals with the results of measurements and either interpretation leads to the same uncertainties in measured quantities.

As anticipated in Chapter 1, another philosophical idea affected by the uncertainty principle was that of causality. According to classical theory, the path of a particle is determined by its initial position and momentum and by the forces acting on it. If the forces between the particles of the universe were

known and if it were possible to measure, at a given time, the exact position and momentum of every particle, then the past and future positions and momenta of every particle could be calculated. The past and future are completely determined by the information known at an instant of time. The uncertainty principle indicates that we cannot know an exact position and momentum for each particle; we can only determine what the particles will probably do. For macroscopic objects the uncertainties are so small that the probable motion does not differ significantly from classical motion. However, for photons and electrons, the classical prediction of their motion gives a poor idea of the experimental results.

5-10 THE DOUBLE-SLIT EXPERIMENT

To crystallize the ideas we have been discussing about the wave-particle duality and to emphasize the limits on our ability to describe the behavior of the basic entities of the physical world, we take the double-slit diffraction experiment mentioned in Section 5-8 for an example. A schematic diagram of the experiment is shown in Fig. 5-11. The source emits a beam which is incident on two slits separated by a distance D . The beam could be electromagnetic, that is, a stream of photons, or a beam of cathode rays, that is, a stream of electrons. The following analysis applies to either, but for convenience we shall consider the stream to be photons. At a distance from the slits which is large, compared to D , we have a detector, which could be a photographic film or a series of photoelectric cells.

If the detector is a film, it will show, after exposure, the characteristic interference pattern indicated by the curve labeled intensity on the figure. The positions of the maxima and minima are found by considering the superposition

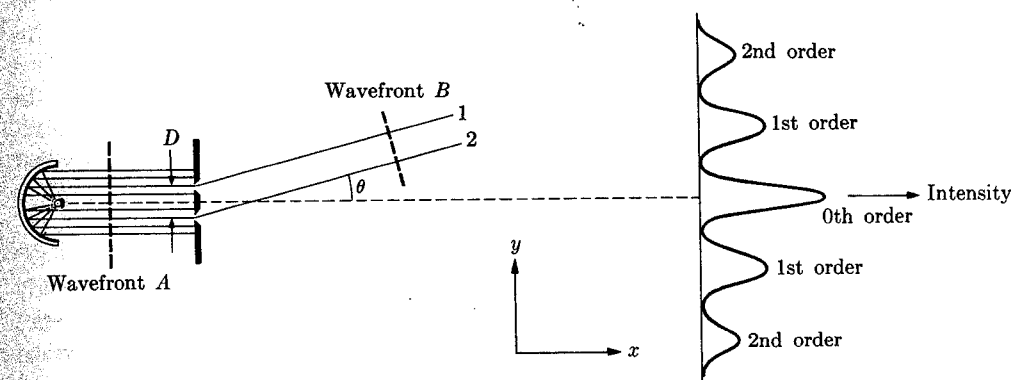


Fig. 5-11 A double-slit diffraction experiment. The distance to the screen is very long compared to the slit separation D .

of the wave from one slit with the other; that is, the interference pattern is a prediction of the wave model.

Rays 1 and 2, which converge to a point on a screen and therefore can interfere with each other, can be considered on the left-hand part of Fig. 5-11 to be virtually parallel, because of the distances involved. From wavefront A to wavefront B is a difference in distance between the two rays of $D \sin \theta$. The angular separation of the central maximum and the adjacent minimum is therefore

$$D \sin \theta = \lambda/2 = h/2p_x,$$

where λ is the wavelength of the light and p_x is the associated momentum of the photon.

When angle θ is small, it becomes

$$\theta = h/2p_x D, \quad (5-53)$$

and θ is the angle between any adjacent maximum and minimum.

If the detector is a series of photoelectric cells, the light will release photoelectrons and the maxima will indicate those cells where many electrons are emitted. Each photoelectron represents the arrival at the detector of a photon and thus more photons strike the detectors around the maxima in the pattern than around the minima. The pattern gives very little information pertaining to a single photon but only the effect produced by many photons. The correlation between the wave model and the particle model is statistical. The maxima of the wave pattern represent regions of greatest probability for the arrival of a photon.

If one of the slits is covered during the experiment, the resulting single-slit pattern will differ from the preceding one. If a cover is placed over the bottom slit for the first half of the experiment and then the cover is placed over the top slit for the second half, the total exposure at the detector is *different* than when both slits are uncovered. The positions on the screen, where the photon will most likely strike, change. If we consider the light beam to be a stream of photons, a single photon must pass through either one slit or the other. The fact that the pattern is different for two slits than for one slit means that the motion of the photon is influenced by the other slit. It appears that the photon, as it passes through one slit, "knows" whether the other slit is open. Thus the particle model seems to lead to an absurd result.

An analysis of the experiment shows that no information was obtained experimentally about the passage of a photon through either slit. Consequently a statement about such passage is meaningless. This emphasizes that physics deals with predictions for experimental results. The definition of every physical quantity *must* contain, explicitly or implicitly, the operation necessary to measure the physical quantity. It makes *no sense* to talk about results which cannot be observed. If we want to know through which slit the photon passes,

we must revise the experiment so that we can determine this. To detect the passage of a photon we place many small particles just to the right of the slits. After passing through a slit, the photon will collide with one of these particles. Observation of the recoil of the small particle will allow us to determine the slit used by the photon. In this ideal experiment the only uncertainties introduced will be those predicted by the uncertainty principle; we will assume that the precision achieved in constructing the apparatus was so high that there are no uncertainties in dimensions, such as the separation of the slits.

To be certain of the slit from which the small particle recoiled, the uncertainty in its y -position must be much smaller than the separation of the slits; we must have

$$\Delta y \ll D.$$

There will be an exchange of momentum during the collision, but there is an uncertainty in the amount since we don't know the details of the collision. The uncertainty in the y -component of the momentum of the photon, Δp_y , must not be great enough to cause it to deviate from the interference pattern. This means that we must have

$$\Delta p_y/p_x \ll \theta = h/2p_x D,$$

or

$$\Delta p_y \ll h/2D.$$

Since momentum is conserved, Δp_y is also the uncertainty in the y -component of the momentum of the small particle. If we multiply the uncertainty in the y -position of the small particle with the uncertainty in its y -component of the momentum, we obtain

$$\Delta y \Delta p_y \ll Dh/2D = h/2. \quad (5-54)$$

If we compare this with the prediction of the uncertainty principle, $\Delta y \Delta p_y \simeq \hbar$, we see that the small uncertainties necessary in Eq. (5-54) are not possible. If Δy is small enough that we can determine through which slit the photon passes, Δp_y is so large that we do not get the interference pattern at the detector. *We cannot detect both the particle nature, as indicated by the collision with the small particle, and the wave nature, as indicated by the interference pattern.* This example also illustrates how the uncertainty principle is used to resolve apparent conflicts between the wave model and the particle model.

5-11 SUMMARY

The wave-particle duality of matter is substantiated by experiment. Neither the wave model nor the particle model is sufficient alone to include all of the properties of the physical world. The two models are synthesized to complement each other in providing a description for all experimental results. This synthesis is contained in the relations between the wave properties of wavelength and frequency and the particle properties of momentum and energy.

The predictions of the two models seem to be correlated statistically; a large wave amplitude means a large probability of the particle being at that position. For material particles like electrons, the particle model has been developed so that, for example, we can calculate electron trajectories in magnetic fields. The corresponding wave model for material particles requires further elaboration. Although we can find the associated wavelength and frequency, we have no method for calculating the amplitude of the "electron wave." Our experience with previous wave motions, such as sound waves, indicates that a wave equation is needed. The solution of this equation would give the amplitude of the wave, which we can correlate with the particle model. A complete acceptance of the dual nature of matter requires a further development of the wave model.

PROBLEMS

5-1 Show that the cross section for Thomson scattering is

$$\sigma_T = \frac{e^4}{6\pi\epsilon_0 m_e^2 c^4} = 6.66 \times 10^{-25} \text{ cm}^2.$$

5-2 X-ray photons of wavelength 0.712 \AA undergo Compton collisions in carbon. What is the wavelength change of the line scattered at 90° if the scattering particle is a) an electron and b) the whole carbon atom?

5-3 Each of three quanta of radiation undergoes a 90° Compton scattering in a block of graphite. Assuming that the ejected electron had no binding energy in carbon, compute the fractional change in wavelength ($\Delta\lambda/\lambda$) for the scattered radiation when the incident quantum is: a) a gamma ray from cobalt, $\lambda = 1.06 \times 10^{-2} \text{ \AA}$; b) x-rays from molybdenum, $\lambda = 0.712 \text{ \AA}$; and c) visible light, $\lambda = 5000 \text{ \AA}$. d) The binding energy of an electron in carbon is actually 4.0 eV . If this is taken into account, what would be the answers to the preceding parts? e) Comment on the feasibility of resolving the two waves in a beam composed of the incident and scattered radiation in each of the preceding cases.

5-4 An x-ray quantum having a wavelength of 0.15 \AA undergoes a Compton collision and is scattered through an angle of 37° . a) What are the energies of the incident and scattered photons and of the ejected electron? b) What is the magnitude of the momentum of each photon? c) Find the momentum of the electron both graphically and analytically using the values found in the preceding part.

5-5 Using the data and results of Problem 5-2 for Compton scattering of $\lambda = 0.712 \text{ \AA}$ photons by carbon, find the energy of the recoil particle given that it is a) an electron and b) the whole carbon atom. c) What is the direction of motion of the recoil particle in each case with respect to the direction of incidence of the photon?

5-6 A photon of energy E undergoes a Compton collision with a free particle of rest mass m_0 . a) Show that the maximum recoil kinetic energy of the particle is

$$E_{k_{\max}} = \frac{E^2}{E + m_0 c^2/2}.$$

b) What is the maximum energy that can be transferred to a free electron by Compton collision of a photon of violet light ($\lambda = 4000 \text{ \AA}$)? c) Could violet light eject electrons from a metal by a Compton collision?

5-7 When a hydrogen atom goes from the state $n = 2$ to the state $n = 1$, the energy of the atom decreases by 10.2 eV . In Chapter 4 it was stated that all of this energy is radiated as a single photon. Actually, the energy of the photon must be slightly less than 10.2 eV , since a small part of the energy is needed to provide the kinetic energy of the recoiling atom. a) What is the recoil momentum of the hydrogen atom? b) What fraction of the 10.2 eV is taken by the recoil of the atom?

5-8 The apparatus for a Compton-scattering experiment is arranged so that the scattered photon and the recoil electron are detected only when their paths are at right angles to one another. Show that under these conditions a) the scattered wavelength is given by $\lambda' = \lambda/\cos \alpha$ and b) the energy of the scattered photon is $m_e c^2$.

5-9 Show that the deBroglie wavelength in angstroms for an electron accelerated from rest through a potential difference V in volts is a) classically $\lambda = 12.27/V^{1/2}$ and b) relativistically

$$\lambda = \frac{12.27}{V^{1/2}} \left(\frac{Ve}{2m_e c^2} + 1 \right)^{-1/2}.$$

5-10 What is the deBroglie wavelength of the waves associated with an electron that has been accelerated from rest through a potential difference of a) 100 V ? b) 8000 V ?

5-11 Show that the deBroglie wavelength for a particle of mass m moving with the rms speed of a Maxwellian distribution at temperature T is $\lambda = h/(3mkT)^{1/2}$, where k is Boltzmann's constant.

5-12 An alpha particle (doubly ionized helium) is ejected from the nucleus of a radium atom with 5.78 MeV of kinetic energy. a) What is the deBroglie wavelength of this particle? b) How does this wavelength compare with the nuclear diameter, which is about $3 \times 10^{-15} \text{ m}$ for the alpha particle?

5-13 a) What is the momentum of a photon of wavelength 0.02 \AA ? b) What is the momentum of an electron that has the same total energy as a 0.02 \AA photon? c) What is the deBroglie wavelength of the electron in part b)?

5-14 Using the rotation vector idea of Section 5-6, add four waves with equal amplitudes and different frequencies to obtain the resultant amplitude as a function of time. Assume that $\omega_1 = 2\pi \text{ rad s}^{-1}$ and $\delta\omega = \pi \text{ rad s}^{-1}$. Plot the amplitude as a function of time for every $\frac{1}{8} \text{ s}$ and show that the time between groups is 2 s and the time duration of the group is 1 s .

Chapter 2

THE SPECIFIC HEAT OF SOLIDS AND LATTICE VIBRATIONS

2-1. The specific heat at constant volume and at constant pressure

According to the first law of thermodynamics, the amount of heat dQ added to a system must be equal to the increase in energy dE of the system plus the amount of work done by the system. In case the work done by the system is of a mechanical nature only, one may thus write

$$dQ = dE + p dV \quad (2-1)$$

Now, E is, except for an arbitrary constant, determined uniquely by the temperature and volume of the system. Hence

$$dE = \left(\frac{\partial E}{\partial T}\right)_V dT + \left(\frac{\partial E}{\partial V}\right)_T dV$$

and (2-1) may be rewritten in the form

$$dQ = \left(\frac{\partial E}{\partial T}\right)_V dT + \left[\left(\frac{\partial E}{\partial V}\right)_T + p\right] dV \quad (2-2)$$

The specific heat in general is defined by dQ/dT , and unless stated otherwise, will be assumed to refer to 1 gram molecule of the solid. However, unless one specifies in which way the increase in temperature takes place, the specific heat is undetermined; in particular one must specify the corresponding change in volume, as is evident from (2-2). Thus there exist an infinite number of specific heats, but in general one is interested in only two: the specific heat at constant volume C_V and the specific heat at constant pressure C_p . According to (2-2), the former is given by

$$C_V = \left(\frac{dQ}{dT}\right)_V = \left(\frac{\partial E}{\partial T}\right)_V \quad (2-3)$$

Theoretically speaking, this is the most interesting quantity, as it is obtained immediately from the energy of the system; most of the following discussions will therefore refer to C_V . From the experimental point of view, however, it is much more convenient to measure the specific heat at constant pressure C_p .

Sec. 2-1]. SPECIFIC HEAT AND LATTICE VIBRATIONS

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a solid at constant pressure than at constant volume. As shown in textbooks on thermodynamics, the second law leads to the following relationship between C_p and C_V :¹

$$C_p - C_V = -T \left(\frac{\partial V}{\partial T}\right)_p^2 \left(\frac{\partial p}{\partial V}\right)_T \quad (2-4)$$

This may be rewritten in terms of the volume expansion coefficient α_V and the compressibility K , defined by

$$\alpha_V = (1/V)(\partial V/\partial T)_p \quad \text{and} \quad K = -(1/V)(\partial V/\partial p)_T \quad (2-5)$$

Expression (2-4) then takes the form

$$C_p - C_V = \alpha_V^2 TV/K \quad (2-6)$$

Thus C_V may be calculated from C_p measurements if at the same time α_V and K are known at the temperature of interest. Since both α_V and K are positive quantities, $C_p - C_V \geq 0$.

By way of illustration, we have given in Fig. 2-1 C_p and C_V as functions of temperature for copper; note that at low temperatures their difference becomes very small and that both go to zero at $T = 0$. It is essentially the temperature variation of the specific heat at constant volume which will be discussed in the present chapter.

It may be noted that if no direct compressibility data are available for the temperature range of interest, one frequently employs the relationship

$$C_p = C_V(1 + \gamma \alpha_V T) \quad \text{with} \quad \gamma = \alpha_V V/KC_V \quad (2-7)$$

The quantity γ is called the Grüneisen constant and is practically independent of temperature.² Thus by calculating γ at some arbitrary temperature from available data, one may obtain an approximation for C_V at other temperatures from a knowledge of the coefficient of volume expansion.

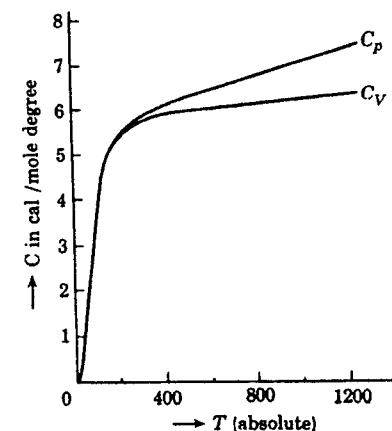


Fig. 2-1. The temperature variation of C_p and C_V for copper. [By permission from M. W. Zemansky, *Heat and Thermodynamics*, 2d ed., McGraw-Hill, New York, 1943, p. 237]

¹ See, for example, M. W. Zemansky, *Heat and Thermodynamics*, 2d ed., McGraw-Hill, New York, 1943, p. 227.

² F. Grüneisen, *Handbuch der Physik*, 10, 1-59 (1926); see also J. C. Slater, *Phys. Rev.*, 57, 744 (1940).

From the atomic point of view one may distinguish between various contributions to the specific heat of solids. In the first place, there is the contribution resulting from the atomic vibrations in the crystal; an increase in temperature is associated with a more vigorous motion of the atoms, which requires an input of energy. Second, in metals and in semiconductors there is an additional contribution to the specific heat from the electronic system. Usually this contribution is small relative to that of the lattice vibrations, as explained in Chapter 9. As the temperature

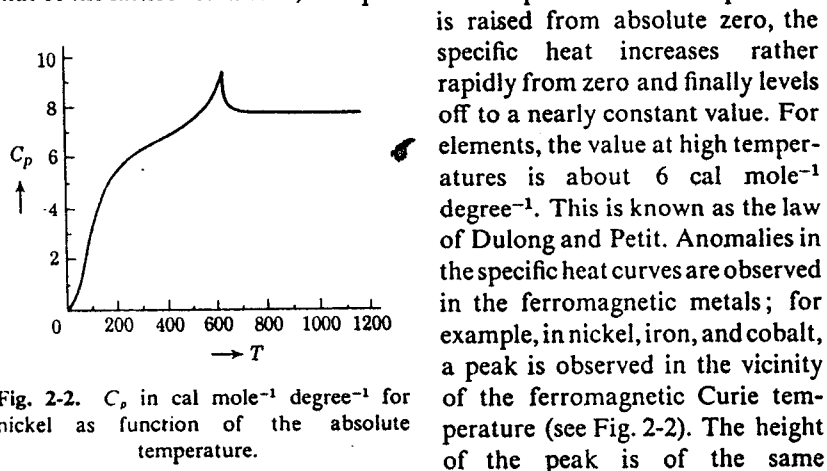


Fig. 2-2. C_p in $\text{cal mole}^{-1} \text{degree}^{-1}$ for nickel as function of the absolute temperature.

is raised from absolute zero, the specific heat increases rather rapidly from zero and finally levels off to a nearly constant value. For elements, the value at high temperatures is about $6 \text{ cal mole}^{-1} \text{degree}^{-1}$. This is known as the law of Dulong and Petit. Anomalies in the specific heat curves are observed in the ferromagnetic metals; for example, in nickel, iron, and cobalt, a peak is observed in the vicinity of the ferromagnetic Curie temperature (see Fig. 2-2). The height of the peak is of the same order of magnitude as the normal specific heat. The peak is associated with the transition from the ferromagnetic (ordered) to the paramagnetic (disordered) state. Similar peaks occur in the specific heat curves of alloys which exhibit order-disorder transitions, and in ferroelectric materials. These anomalies are discussed in the relevant chapters; in the present chapter the discussion is confined to the specific heat associated with atomic vibrations.

2-2. The various theories of the lattice specific heat

In Sec. 2-10 it will be shown that the vibrational energy of a linear chain of N atoms may be expressed as the energy of N harmonic oscillators. Extending the arguments employed there to the three-dimensional case, one is led to the conclusion that:

The vibrational energy of a crystal containing N atoms is equivalent with the energy of a system of $3N$ harmonic oscillators.

This feature is common to all theories of the specific heat and the distinction between the various theories is based on their differences in the proposed frequency spectrum of the oscillators. The central problem in the theory of the specific heat is therefore the calculation of the

wavelengths and frequencies of the possible modes of vibration of the crystal under consideration. The different approaches to this problem will be outlined below.

With regard to the harmonic oscillator representation referred to above, the following qualitative remarks may provide some clarification. Suppose it were possible to fix the position of all the nuclei in a crystal such that they are all in their equilibrium position. If one of the nuclei were now displaced over a distance small compared with the shortest interatomic distances, and then set free again, the displaced atom would carry out harmonic vibrations about its equilibrium position, and its energy of vibration would be the same as that of three one-dimensional harmonic oscillators, one for each direction of motion. Applying the same reasoning to the other atoms in the crystal, one arrives at a system of $3N$ harmonic oscillators representing the vibrations of the crystal as a whole.

2-3. The breakdown of the classical theory

The energy of a harmonic oscillator of natural angular frequency ω may be written

$$\epsilon = p^2/2m + m\omega^2 q^2/2 \quad (2-8)$$

where the first term on the right represents the kinetic energy (p is the momentum) and the second term represents the potential energy (q is the deflection from the equilibrium position). It is well known that the average energy of a harmonic oscillator according to classical statistical mechanics is given by

$$\langle \epsilon \rangle = \int_0^\infty \epsilon e^{-\epsilon/kT} d\epsilon / \int_0^\infty e^{-\epsilon/kT} d\epsilon = kT \quad (2-9)$$

where T is the absolute temperature and k is Boltzmann's constant. It is important to note that the frequency does not enter in this result. In other words, the vibrational energy of a crystal of N atoms is classically always equal to

$$E = 3NkT \quad (2-10)$$

independent of the assumed frequency distribution of the oscillators used in the model. Now, as long as the volume of the solid is kept constant, (2-10) is the only temperature-dependent contribution to the total energy of the system. Thus, for a solid containing one type of atoms and putting N equal to the number of Avogadro, one obtains for the specific heat per gram atom,

$$C_V = 3Nk = 3R = 5.96 \text{ cal degree}^{-1} \text{ mole}^{-1} \quad (2-11)$$

where R is the gas constant. Similarly, if the solid consists of N atoms A and N atoms B, the specific heat per mole would be $6R$, etc. The result

obtained is in quantitative agreement with experiment (if sources of the specific heat other than lattice vibrations are subtracted) at high temperatures only. In other words, it does not explain the decrease of the specific heat at low temperatures, as observed for all solids. This discrepancy is essentially removed when quantum theory is used, as will be seen below. It may be noted that the classical theory led to similar difficulties in the specific heat of molecules.

2-4. Einstein's theory of the specific heat

A great step forward toward an understanding of the specific heat curves at low temperatures was made by Einstein in 1906.³ Although the physical model employed by Einstein was oversimplified, his results definitely indicated that quantum theory contained the answer to the difficulty encountered in the classical theory. He assumed that a solid element, containing N atoms, could be represented by $3N$ harmonic oscillators of the same frequency ν . This model implies that the atoms vibrate independently of each other, their frequencies being the same because of their assumed identical surroundings. For the average energy of an oscillator Einstein made use of a result obtained by Planck in 1900, in connection with the theory of black-body radiation. According to Planck, a harmonic oscillator does not have a continuous energy spectrum, as assumed in the classical theory, but can accept only energy values equal to an integer times $h\nu$, where h is Planck's constant. The possible energy levels of an oscillator may thus be represented by⁴

$$\epsilon_n = nh\nu \quad n = 0, 1, 2, 3, \dots \quad (2-12)$$

By replacing the integrals appearing in (2-9) by summations, one thus obtains for the average energy the expression

$$\langle \epsilon \rangle = \frac{\sum_{n=0}^{\infty} nh\nu e^{-nh\nu/kT}}{\sum_{n=0}^{\infty} e^{-nh\nu/kT}} \quad (2-13)$$

To evaluate this expression, first consider the denominator

$$S = \sum_{n=0}^{\infty} e^{-nh\nu/kT} = (1 - e^{-h\nu/kT})^{-1}$$

Differentiating with respect to $1/kT$, one obtains

$$\frac{\partial S}{\partial(1/kT)} = - \sum_{n=0}^{\infty} nh\nu e^{-nh\nu/kT} = - \frac{h\nu e^{-h\nu/kT}}{(1 - e^{-h\nu/kT})^2}$$

It is observed that the expression in the center is identical with the

³ A. Einstein, *Ann. Physik*, **22**, 180, 800 (1906); **34**, 170 (1911).

⁴ See any *Introduction to Modern Physics*.

numerator in (2-13). Substitution into (2-13) thus leads to the well-known Planck formula for the average energy of an oscillator at a temperature T :

$$\langle \epsilon \rangle = \frac{h\nu}{e^{h\nu/kT} - 1} \quad (2-14)$$

We emphasize that in contrast with (2-9), this expression contains the frequency of the oscillator. The temperature dependence of $\langle \epsilon \rangle$ is illustrated in Fig. 2-3, showing $\langle \epsilon \rangle/kT$ as function of $h\nu/kT$. Note that at high temperatures $\langle \epsilon \rangle \simeq kT$, in agreement with the classical theory. However, at low temperatures, $\langle \epsilon \rangle$ decreases exponentially to zero. In the Einstein model, the vibrational energy of a solid element containing N atoms is thus equal to

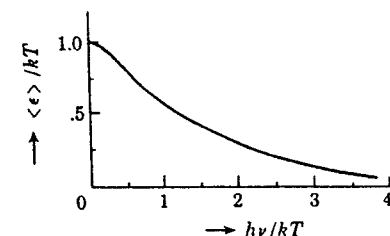


Fig. 2-3. The average energy in units of kT of a harmonic oscillator of frequency ν as a function of $h\nu/kT$, according to Planck.

$$E = 3N\langle \epsilon \rangle = 3N \frac{h\nu}{e^{h\nu/kT} - 1} \quad (2-15)$$

The specific heat at constant volume is therefore per mole

$$C_V = \frac{\partial}{\partial T} E = 3R \left(\frac{h\nu}{kT} \right)^2 \frac{e^{h\nu/kT}}{(e^{h\nu/kT} - 1)^2} \quad (2-16)$$

Before discussing this result, it may be remarked that according to quantum mechanics, the possible energy levels of a harmonic oscillator are given by

$$\epsilon_n = (n + \frac{1}{2})h\nu \quad n = 0, 1, 2, \dots \quad (2-17)$$

rather than by (2-12).⁵ This has the effect of shifting all energy levels by the constant amount of $h\nu/2$, and instead of (2-14), one obtains

$$\langle \epsilon \rangle = \frac{h\nu}{2} + \frac{h\nu}{e^{h\nu/kT} - 1} \quad (2-18)$$

The first term is called the zero-point energy of the oscillator because $\langle \epsilon \rangle = h\nu/2$ for $T = 0$. Thus, according to quantum mechanics, the atoms have vibrational energy even at absolute zero. The expression for the specific heat is not altered by this result, because C_V is determined by the derivative of $\langle \epsilon \rangle$ with respect to T .

With regard to (2-16) it is observed that for $kT \gg h\nu$, this expression reduces in first approximation to the classical result (2-11). At low temperatures, however, the specific heat decreases. To discuss this

⁵ For a proof see any introduction to wave mechanics.

behavior, it is convenient to introduce the Einstein temperature θ_E , defined by

$$h\nu = k\theta_E \quad (2-19)$$

Expression (2-16) may then be written in the form

$$\frac{C_V}{3R} = \left(\frac{\theta_E}{T}\right)^2 \frac{e^{\theta_E/T}}{(e^{\theta_E/T} - 1)^2} = F_E \left(\frac{\theta_E}{T}\right) \quad (2-20)$$

where F_E is called the Einstein function; it determines the ratio of the

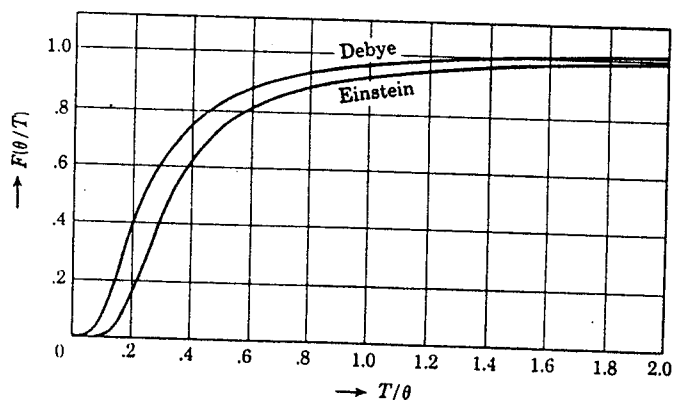


Fig. 2-4. The Debye and Einstein functions as function of T/θ .

specific heat at a temperature T and the classical (high-temperature) value $3R$. The Einstein function is represented in Fig. 2-4, together with the Debye function, which will be discussed in Sec. 2-6. We see that the curve obtained has the same appearance as the observed specific heat curves. On the other hand, the Einstein curve deviates from the experimentally observed ones in the region of low temperatures. Experimentally, it is found that for most solids the lattice specific heat at very low temperatures (liquid helium) is proportional to T^3 . However, for $T \ll \theta_E$, equation (2-20) leads to a specific heat proportional to $\exp(-\theta_E/T)$. In other words, the Einstein function falls off more rapidly at low temperatures than it should. The reason for this discrepancy must be sought in the oversimplified model employed by Einstein. In fact, we shall see in the next sections that rather than a single frequency ν , the vibrational spectrum of a solid covers a wide range of frequencies. This, in turn, is a result of the fact that the atomic vibrations in a crystal are strongly coupled and cannot be considered independent. On the other hand, because of its simplicity, the Einstein model is frequently used in problems in which lattice vibrations play a role.

2-5. The vibrational modes of a continuous medium

In the preceding section it was pointed out that the discrepancy between the Einstein theory and experimental results in the low temperature region was a consequence of the oversimplified model employed by Einstein. In 1912, Debye tackled the problem from a different point of view and, as we shall see, with great success.⁶ Debye realized that it is possible to propagate waves through solids covering a wavelength region extending from low frequencies (sound waves) up to short waves (infrared absorption). The essential difference between the Debye model and the Einstein model is that Debye considers the vibrational modes of a crystal as a whole, whereas Einstein's starting point was to consider the vibration of a single atom, assuming the atomic vibrations to be independent of each other.

In the present section, we shall deal with the vibrational modes of a continuous medium, because the results are basic to the "continuum theories" of the specific heat. Let us first consider for simplicity the vibrational modes of a one-dimensional continuous string of length L . Suppose $u(x,t)$ represents the deflection of the string at the point x at the instant t . The waves may then be described by the one-dimensional wave equation

$$\frac{\partial^2 u}{\partial x^2} = \frac{1}{c_s^2} \frac{\partial^2 u}{\partial t^2} \quad (2-21)$$

where c_s is the velocity of propagation of the waves. If it is assumed that the end points of the string are fixed, the solutions of (2-21) are those corresponding to standing waves:

$$u(x,t) = A \sin(n\pi x/L) \cos 2\pi\nu_n t \quad (2-22)$$

where n is a positive integer ≥ 1 . The wavelengths and frequencies of the possible vibrations represented by (2-22) are given by

$$\lambda_n = 2L/n \quad \text{and} \quad \nu_n = c_s/\lambda_n = c_s n/2L \quad (2-23)$$

The frequency spectrum is discrete, one frequency corresponding to each integer value n . Note that for the one-dimensional string the frequency spectrum corresponds to an infinite number of equidistant lines, as illustrated in Fig. 2-5a. The number of possible modes of vibration in a frequency interval $d\nu$ is, on the average, equal to

$$dn = (2L/c_s) d\nu \quad (2-24)$$

In the three-dimensional case, the wave equation reads

$$\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} + \frac{\partial^2 u}{\partial z^2} = \frac{1}{c_s^2} \frac{\partial^2 u}{\partial t^2} \quad (2-25)$$

⁶ P. Debye, *Ann. Physik*, 39, 789 (1912)

Assuming a continuous medium in the shape of a cube of edge L and assuming the faces of the cube to be fixed, the possible standing wave solutions are, in analogy with (2-22),

$$u(x, y, z, t) = A \sin(n_x \pi x / L) \sin(n_y \pi y / L) \sin(n_z \pi z / L) \cos 2\pi \nu t \quad (2-26)$$

where now n_x , n_y , and n_z are positive integers ≥ 1 . Substituting this solution into the differential equation (2-25), one obtains the following expression for the possible modes of vibration:

$$(\pi^2/L^2)(n_x^2 + n_y^2 + n_z^2) = 4\pi^2\nu^2/c_s^2 = 4\pi^2/\lambda^2 \quad (2-27)$$

Thus the possible wavelengths and frequencies are determined by three integers in this case. Let us now ask the question: What is the number

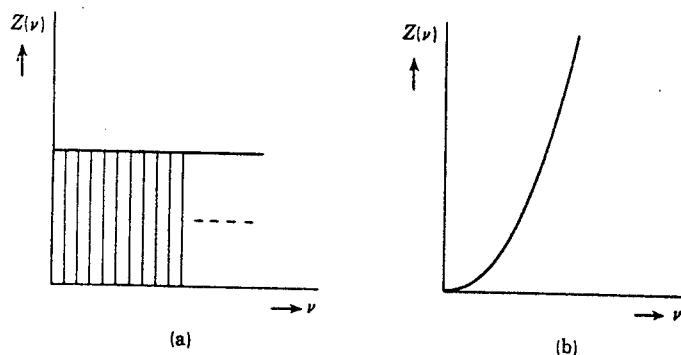


Fig. 2-5. (a) Frequency spectrum for a finite continuous string, according to (2-24). (b) Frequency spectrum for a three-dimensional continuum, according to (2-30).

of possible modes of vibrations $Z(\nu) d\nu$ in the frequency interval between ν and $\nu + d\nu$? To answer this, consider a network of points, each point being determined by three Cartesian positive integer coordinates n_x , n_y , and n_z . Writing

$$R^2 = n_x^2 + n_y^2 + n_z^2 = 4L^2\nu^2/c_s^2 \quad (2-28)$$

it is evident that the number of points in a shell between R and $R + dR$ is equal to⁷

$$\frac{1}{2} 4\pi R^2 dR \quad (2-29)$$

⁷ Each point occupies on the average a unit volume in the integer space.

Now, each point corresponds to a set of three integers n_x , n_y , n_z , and each set of integers determines, according to (2-26), a possible mode of vibration; hence (2-29) immediately gives the number of possible modes of vibration in a given range. Expressing R in terms of ν in (2-29) one thus finds

$$Z(\nu) d\nu = (4\pi V/c_s^3) \nu^2 d\nu \quad (2-30)$$

where V is the volume of the solid. For a perfect continuum, the possible frequencies vary between 0 and ∞ , the number of such possible vibrations increasing with the square of the frequency (see Fig. 2-5b). This situation holds, for example, in the case of electromagnetic waves in a box of volume V . Expression (2-30) is therefore basic in the theory of black-body radiation.

In the case of elastic waves, we may distinguish between transverse and longitudinal waves. In general, the velocities of propagation, say c_t and c_l , respectively, will not be equal. To set up an expression for $Z(\nu) d\nu$ in this case one should keep in mind that for each frequency or wavelength there are two transverse modes and one longitudinal mode.⁸ Thus, instead of (2-30) one obtains

$$Z(\nu) d\nu = 4\pi V \left(\frac{2}{c_t^3} + \frac{1}{c_l^3} \right) \nu^2 d\nu \quad (2-31)$$

How this expression has been used in the theory of the specific heat of solids will be discussed in the following two sections.

2-6. The Debye approximation

One may wonder what the discussion of the preceding section could have to do with the specific heat of crystals, which are by no means continuous but are built up of atoms, i.e., of discrete "mass points." The reason is the following: Consider an elastic wave propagated in a crystal of volume V . As long as the wavelength of the wave is large compared with the interatomic distances, the crystal "looks like" a continuum from the point of view of the wave. The essential assumption of Debye is now that this continuum model may be employed for all possible vibrational modes of the crystal. Furthermore, the fact that the crystal actually consists of atoms is taken into account by limiting the total number of vibrational modes to $3N$ (see Sec. 2-2), N being the total number of atoms. In other words, the frequency spectrum corresponding to a perfect continuum is cut off so as to comply with a total of $3N$ modes (see Fig. 2-6a). The Debye cut-off procedure leads to a maximum

⁸ In the longitudinal modes, the deflection is along the direction of propagation; in the transverse modes the deflection is perpendicular to the direction of propagation, which gives two independent components.

frequency ν_D (the Debye frequency) common to the transverse and longitudinal modes; it is defined by

$$\int_0^{\nu_D} Z(\nu) d\nu = 4\pi V \left(\frac{2}{c_t^3} + \frac{1}{c_l^3} \right) \int_0^{\nu_D} \nu^2 d\nu = 3N \quad (2-32)$$

or

$$\nu_D^3 = \frac{9N}{4\pi V} \left(\frac{2}{c_t^3} + \frac{1}{c_l^3} \right)^{-1} \rightarrow \frac{3N \bar{c}^3}{4\pi V} \quad (2-33)$$

where $Z(\nu)$ as given by (2-31) has been used. It should be noted that this procedure assumes that the velocities c_t and c_l are independent of the

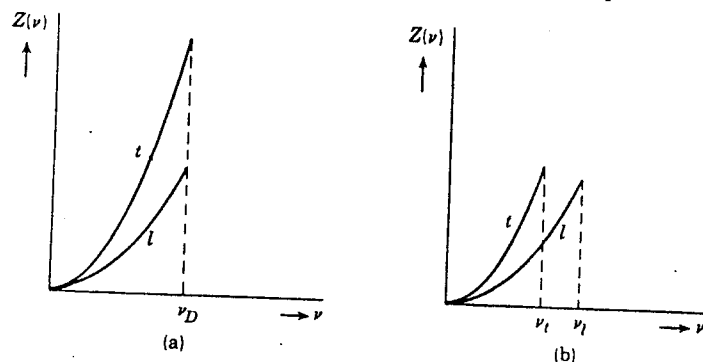


Fig. 2-6. The Debye cut-off takes place at the Debye frequency ν_D , common to the transverse and longitudinal modes (a). In Born's procedure, the cut-off takes place at a common minimum wavelength, corresponding to the maximum frequencies ν_t and ν_l for the transverse and longitudinal modes respectively (b). Note that $c_t < c_l$.

wavelength, as in the continuum. It will be seen in Sec. 2-9 that this is not correct for actual crystals. The order of magnitude of ν_D may be obtained by taking $N/V \simeq 10^{22}$ per cm^3 and using for the velocity of sound $\sim 10^3$ cm sec^{-1} . This gives $\nu_D \simeq 10^{13}$ per second. This corresponds to a minimum wavelength of the order of one Angstrom, indicating that the continuum theory may be at fault, especially in the high-frequency region.

Associating with each vibrational mode a harmonic oscillator of the same frequency, one finds from (2-31) and Planck's formula (2-14) for the vibrational energy of the crystal,

$$E = \int_0^{\nu_D} Z(\nu) \frac{h\nu}{e^{h\nu/kT} - 1} d\nu = 9N \left(\frac{kT}{h\nu_D} \right)^3 kT \int_0^{x_m} \frac{x^3 dx}{e^x - 1} \quad (2-34)$$

where $x = h\nu/kT$ and $x_m = h\nu_D/kT$. Here, as in the Einstein theory, it is convenient to introduce a characteristic temperature; thus one defines the Debye temperature as

$$\theta_D = h\nu_D/k \quad (2-35)$$

The upper limit of integration is then equal to $x_m = \theta_D/T$. It is observed that for high temperatures ($T \gg \theta_D$), x is small compared with unity for the whole range of integration. In that case, the denominator of the integrand in (2-34) may be replaced in first approximation by x . This yields for the specific heat,

$$C_V = \partial E / \partial T = 3Nk \quad \text{for } T \gg \theta_D$$

a result identical with the classical theory.

In the case of very low temperatures, such that $T \ll \theta_D$, the upper limit of integration in (2-34) may be replaced by infinity. Now,⁹

$$\int_0^\infty \frac{x^3 dx}{e^x - 1} = 6 \sum_{n=1}^\infty \frac{1}{n^4} = \frac{\pi^4}{15}$$

so that

$$E = \frac{3}{8} \pi^4 NkT (T/\theta_D)^3 \quad \text{for } T \ll \theta_D \quad (2-36)$$

Thus the energy of vibration is proportional to T^4 at low temperatures (for the theory of black-body radiation, which may be treated in a completely analogous way, this is the case at any temperature, because there the upper limit to the frequency does not exist). The specific heat at low temperatures according to Debye is thus given by

$$C_V = \frac{1}{8} \pi^4 Nk (T/\theta_D)^3 \quad \text{for } T \ll \theta_D \quad (2-37)$$

This is the famous Debye T^3 law, which should hold for $T < \theta_D/10$. The general expression for the specific heat as function of temperature may be obtained by differentiating (2-34) with respect to T . For 1 mole of substance one obtains in this way

$$C_V = 3R \cdot 3 \left(\frac{T}{\theta_D} \right)^3 \int_0^{\theta_D/T} \frac{e^x x^4}{(e^x - 1)^2} dx = 3R F_D \left(\frac{\theta_D}{T} \right) \quad (2-38)$$

where F_D is the Debye function. It has been represented in Fig. 2-4 together with the Einstein function. The reason that the Debye curve lies above the Einstein curve is a result of the fact that in the Debye model, the low-frequency modes are taken into account; at low temperatures these have a higher average energy and temperature derivative than the relatively high-frequency Einstein oscillators, as is evident from the Planck formula (2-14).

To illustrate the agreement between the Debye theory and experimentally observed specific heat curves, we reproduce in Fig. 2-7 measurements on silver fitted to a Debye curve. From such curves it is possible

⁹ E. T. Whittaker and G. N. Watson, *Modern Analysis*, 4th ed., Cambridge, London, 1935, p. 265.

to calculate the Debye temperature of the solid involved. Some typical examples are given in Table 2-1.

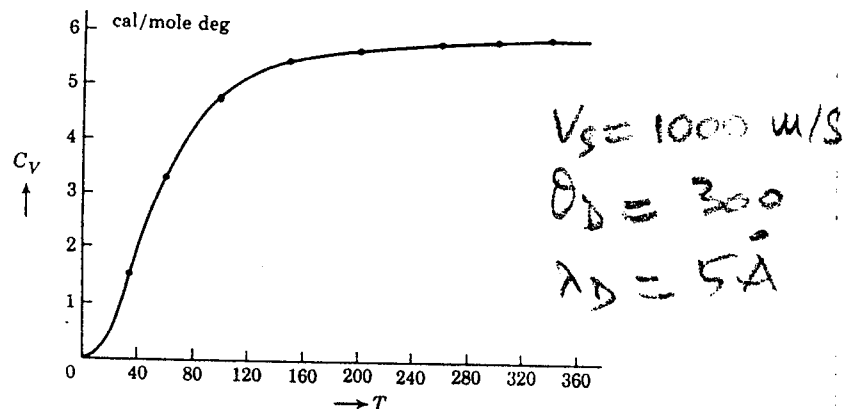


Fig. 2-7. Comparison of the Debye specific heat curve and observed values (dots) for silver; the ordinate is in cal mole⁻¹ degree⁻¹.

Table 2-1. Debye Temperature in Degrees Absolute for a Number of Solids

Solid	θ_D	Solid	θ_D	Solid	θ_D
Na	150	Fe	420	C (diam.)	1860
K	100	Co	385	NaCl	281
Cu	315	Ni	375	KCl	230
Ag	215	Al	390	KBr	177
Au	170	Ge	290	AgCl	183
Be	1000	Sn	260	AgBr	144
Mg	290	Pb	88	CaF ₂	474
Zn	250	Pt	225		
Cd	172				

Notwithstanding the great success of the Debye approximation, accurate measurements in the low-temperature region show deviations from the theoretical predictions. According to the Debye theory, the T^3 law should hold in the temperature region $T \leq 0.1\theta_D$. That this is not always the case may be seen from some examples given in Table 2-2, reproduced from Blackman's paper.¹⁰

The θ_D values given in the table are calculated from (2-37) and should be constant if the T^3 law was satisfied. Similar deviations have been found in other materials. There seems little doubt that these deviations

Table 2-2. Deviations from the T^3 Law

NaCl			KCl			Li		
T	θ_D	$10^3 C_V/T^3$	T	θ_D	$10^3 C_V/T^3$	T	θ_D	$10^3 C_V/T^3$
20	288	0.388	14	213	0.960	30	356	0.101
15	297	0.356	8	222	0.832	20	340	0.118
10	308	0.334	4	236	0.708	15	328	0.131
			3	227	0.798			

are a result of the deficiencies of the continuum approximation, a conclusion which is supported by the work of Blackman and Kellermann,¹¹ the results of which will be briefly discussed in Sec. 2-13. According to Blackman one may expect the T^3 law to hold for the temperature region

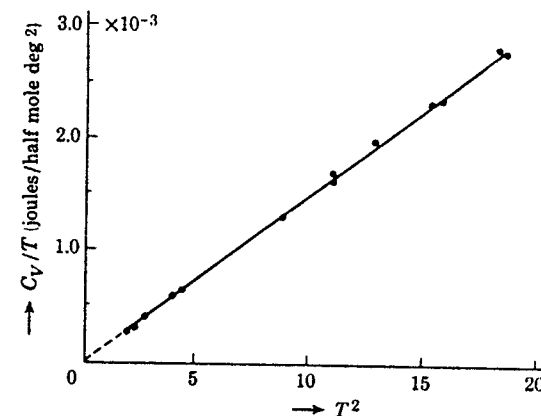


Fig. 2-8. Comparison of the T^3 law and observed values for KCl. [After P. H. Keesom and N. Pearlman, ref. 12]

$T \leq \theta_D/50$, i.e., at considerably lower temperatures than predicted by the Debye approximation. The T^3 law is illustrated in Fig. 2-8 for KCl, representing results obtained by Keesom and Pearlman.¹²

2-7. The Born cut-off procedure

A modification of the Debye theory was introduced by Born, who proposed a different cut-off procedure. In the preceding section it was

¹¹ E. W. Kellermann, *Phil. Trans.*, A238, 513 (1940); *Proc. Roy. Soc.*, A178, 17 (1941).

noted that in the Debye theory, the maximum frequency ν_D was common to both the longitudinal and the transverse modes. Born proposed to cut off the spectrum in such a manner that the longitudinal and transverse modes have a *common minimum wavelength*. This, as will become evident from the discussion in the following sections, is actually more sound theoretically speaking and in line with the theory of lattice vibrations developed by Born and von Karman.¹³ Thus if one takes the common minimum wavelength equal to

$$\lambda_{\min} = (4\pi V/3N)^{1/3} \quad (2-39)$$

one obtains two Debye frequencies, one for the longitudinal modes and one for the transverse modes, viz.,

$$\nu_l = c_l(3N/4\pi V)^{1/3} \quad \text{and} \quad \nu_t = c_t(3N/4\pi V)^{1/3} \quad (2-40)$$

That this procedure leaves the total number of vibrational modes equal to $3N$ follows immediately from (2-31) and (2-40), because

$$4\pi V \left(\int_0^{\nu_l} \frac{2}{c_l^3} \nu^2 d\nu + \int_0^{\nu_t} \frac{1}{c_t^3} \nu^2 d\nu \right) = 3N$$

The frequency distribution according to this cut-off procedure is represented in Fig. 2-6b and may be compared with that used by Debye. We leave it up to the reader to show that Born's modification leads to the following expression for the specific heat:

$$C_V = R[F_D(\theta_l/T) + 2F_D(\theta_t/T)] \quad (2-41)$$

This expression should be compared with (2-38); θ_l and θ_t are the Debye temperatures corresponding to the longitudinal and transverse modes. Apart from the different cut-off procedure, the model is open to the same objections as the Debye theory.

2-8. Elastic waves in an infinite one-dimensional array of identical atoms

The weakest point in the model employed in the Debye theory is the assumption that the continuum representation of a crystal holds for all possible elastic waves. In fact, we have seen that the minimum wavelength is of the same order of magnitude as the interatomic distances and we may thus expect that a more rigorous treatment might give different results, especially in the high-frequency region. In the present and the following sections we shall therefore discuss the principles of finding the possible modes of vibration of atomic lattices. The original work is due

¹³ M. Born, *Atomtheorie des festen Zustandes*, Leipzig (1923); M. Born and Th. von Karman, *Phys. Z.*, **13**, 297 (1912); **14**, 15 (1913).

to Born and von Karman¹³ and to Blackman.¹⁰ To begin with, consider an array of equidistant mass points as represented in Fig. 2-9; the particles

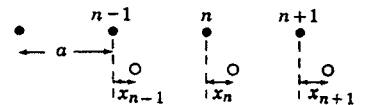


Fig. 2-9. Linear chain of identical mass points. The black dots represent the equilibrium positions, the open circles the displaced particles.

all have a mass m , and for the moment the array will be considered infinitely long. It will be assumed that there exists interaction only between nearest neighbors and that Hooke's law is obeyed.¹⁴ In equilibrium let the distance between neighboring particles be a ; the deflections from the equilibrium position will be denoted by $x_0, x_1, x_2, \dots, x_{n-1},$

x_n, x_{n+1}, \dots . The equation of motion of particle n is then

$$m\ddot{x}_n = -f(x_n - x_{n-1}) - f(x_n - x_{n+1}) = f(x_{n-1} + x_{n+1} - 2x_n) \quad (2-42)$$

where f is the force constant describing the nearest neighbor interaction. We may try to solve this equation by a running wave of the type

$$x_n(t) = e^{-i\omega(t - na/c_s)} = e^{-i(\omega t - qna)} \quad (2-43)$$

where c_s is the velocity of propagation of the wave, $q = \omega/c = 2\pi/\lambda$ is the wave vector and na the equilibrium position of particle n relative to the origin. Substituting this solution into the differential equation (2-42), one obtains after dividing through by x_n ,

$$m\omega^2 = -f(e^{-iqa} + e^{iqa} - 2) = 4f \sin^2(qa/2) \quad (2-44)$$

or

$$\omega = \omega_{\max} \sin(qa/2) \quad \text{with} \quad \omega_{\max}^2 = 4f/m$$

We have thus obtained an expression for the frequency of the waves in terms of the wave vector q , i.e., in terms of the wavelength. To each wave vector q corresponds a frequency ω_q . The relationship has been represented in Fig. 2-10, curve a . It is important to note that for a continuous string, the frequency ν would be equal to $qc_s/2\pi$, i.e., ν would be proportional to the wave vector q as illustrated by curve b in Fig. 2-10. We are thus led to the conclusion that a continuous string and an array of mass points give identical results only if $qa \ll 1$, i.e., when the wavelength is large compared with the interatomic distance. This we had expected. The difference between a continuous string and an array of mass points may also be expressed in this way: the velocity of propagation in a continuous string is independent of the wavelength, whereas in an array of mass points the velocity of propagation becomes smaller as the

¹⁴ For a more general treatment, see L. Brillouin, *Wave Propagation in Periodic Structures*, Dover, New York, 1953.

wavelength decreases. It is evident that this result must have a bearing on the theory of the specific heat, because in the continuum models it was assumed that c_s is a constant.

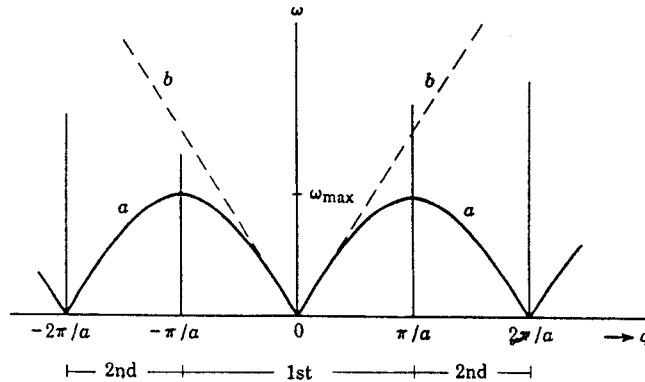


Fig. 2-10. Frequency of elastic waves in a mono-atomic linear lattice as function of the wave vector q . The dashed lines correspond to a continuous string. The first and second Brillouin zones are indicated.

Another important result which follows from the above discussion may be obtained by comparing the solution (2-43) with another in which q has been replaced by

$$q_m = q + 2\pi m/a \quad \text{with } m = \pm 1, \pm 2, \dots \quad (2-45)$$

First of all, it follows from (2-44) that the frequencies corresponding to the modes q and q_m are identical. From this, and from the fact that $\exp(2\pi im) = 1$, it then follows that the solutions (2-43) with q and q_m are identical. In other words, the state of vibration of the array of mass points corresponding to a wave vector q is the same as that for any of the wave vectors $q + 2\pi m/a$. In order to obtain a unique relationship between the state of vibration of the lattice and the wave vector q , the latter must be confined to a range of values $2\pi/a$. Usually one chooses the range such that

$$-\pi/a \leq q \leq \pi/a \quad (2-46)$$

The positive q values correspond to waves propagated in one direction, the negative q values represent waves going in the opposite direction (see 2-43). It also follows from the above discussion that the frequency is a periodic function of q , as illustrated in Fig. 2-10. The region of q values defined by (2-46) is referred to as the first Brillouin zone. The second zone consists of two intervals of half a period each, one on each side of

the first zone as indicated in Fig. 2-10. Higher-order zones are defined in a similar manner.

It is interesting to note that according to (2-44) there exists a maximum frequency ν_{\max} which can be propagated through the chain, viz.,

$$\nu_{\max} = \frac{1}{\pi} \left(\frac{f}{m} \right)^{1/2} \quad (2-47)$$

The chain may thus be considered a low-pass filter which transmits only in the frequency range between zero and ν_{\max} . In contrast with this, the continuous string has no frequency limit. The maximum frequency of the chain of atoms occurs when the wave vector is equal to π/a , i.e., for a wavelength $\lambda_{\min} = 2a$. Now $a \simeq 10^{-8}$ cm and the velocity of sound in solids is of the order of 10^5 – 10^6 cm sec $^{-1}$; this gives $\nu_{\max} \simeq 10^{13}$ sec $^{-1}$.

2-9. Vibrational modes of a finite one-dimensional lattice of identical atoms

In the preceding section the discussion referred to an infinite lattice; in the present section we shall see how the boundary conditions required for a finite lattice lead in a natural manner to an enumeration of the possible modes of vibration. The boundary conditions may be introduced in either of two ways, which will now be discussed:

1. *Boundary conditions leading to standing waves.* Consider an array of $(N + 1)$ similar atoms, numbered from zero to N . Suppose the two end atoms are fixed, so that $(N - 1)$ atoms are mobile. The general solution of the equation of motion (2-42) for a single wavelength may be written as the sum of two running waves, one propagating to the right, the other to the left:

$$x_n(t) = (A_1 e^{iqna + i\beta_1} + A_2 e^{-iqna + i\beta_2}) e^{-i\omega t} \quad (2-48)$$

Here A_1 and A_2 are amplitudes, and β_1, β_2 are phase angles. The boundary conditions are

$$x_0(t) = 0 \quad \text{and} \quad x_N(t) = 0 \quad \text{for all } t$$

The first of these, when substituted in (2-48), requires $A_1 = -A_2$ and $\beta_1 = \beta_2$. Since the phase angles are equal, we shall choose $\beta_1 = \beta_2 = 0$. Taking the real part of the remaining solution, one obtains

$$x_n(t) = 2A_1 \sin qna \sin \omega t \quad (2-49)$$

which represents a standing wave. These solutions lead to the same relationship between ω and q as the running wave solutions, viz., to (2-44). Furthermore, q is now limited to positive values ranging from 0 to π/a . The second boundary condition imposed on (2-49) selects a discrete set of q values, viz., those which satisfy the condition

$$\sin qNa = 0 \quad \text{or} \quad q = (\pi/Na)j \quad (2-50)$$

where j is an integer. Note that $j = 0$ must be excluded, since this corresponds to $q = 0$, i.e., all particles are at rest. The maximum value of q , viz., π/a gives $j_{\max} = N$; however, this value must be excluded for the same reason as $j = 0$. We thus conclude that

$$j = 1, 2, 3, \dots, (N - 1) \quad (2-51)$$

In other words, *there are just as many modes of vibration (q -values) as there are mobile atoms.*

To each value of q there corresponds a value of the frequency ω_q . Hence the frequency spectrum consists of $(N - 1)$ discrete lines. For macroscopic chain lengths the spacing of the lines is so close that we may speak of a quasi-continuous spectrum.

2. Another way of introducing the boundary conditions has been proposed by Born and von Karman; they are called *cyclic* or *periodic boundary conditions* and they are very convenient in the running-wave representation of the vibrational modes. Suppose for a moment we had a circularly shaped chain of atoms, the interatomic separation being a . Let the length of the chain be $L = Na$, where the number of atoms $N \gg 1$. If the atoms are numbered $1, 2, 3, \dots, N$ going around the circle, the boundary condition that applies here is

$$x_n(t) = x_{n+N}(t) \quad (2-52)$$

because the subscripts n and $n + N$ refer to the same particle. Applying this to the running wave (2-43), this condition may be written

$$e^{iqna} = e^{iq(n+N)a} \quad \text{or} \quad q = (2\pi/Na)g = (2\pi/L)g \quad (2-53)$$

where g is an integer. Now, in accordance with (2-46), q is confined to the region between $-\pi/a$ and π/a . In other words, the possible values for g are

$$g = \pm 1, \pm 2, \pm 3, \dots, \pm N/2 \quad (2-54)$$

(the value $g = 0$ gives $q = 0$, corresponding to all particles at rest; this value must therefore be omitted). The total number of different g values (or q values) is thus equal to N . We are thus led to the same conclusion as arrived at under (1), viz., that the number of possible vibrational modes of a chain of atoms is equal to the number of atoms which are free to move. In the running-wave picture, however, q can accept positive as well as negative values; in the standing-wave representation q is always positive. Here again, the frequency spectrum forms a discrete set of lines. The number of possible modes in a wave vector interval dq in the case of the running wave representation is, according to (2-53) equal to

$$dg = (L/2\pi) dq \quad (2-55)$$

In the standing wave representation the corresponding number is, according to (2-50),

$$dj = (L/\pi) dq \quad (2-56)$$

In (2-55), q ranges from $-\pi/a$ to π/a , in (2-56), from 0 to π/a . This accounts for the difference of a factor 2 in the two expressions, the total number of vibrational modes being the same for the two representations.

Actually, one is, of course, not particularly interested in circular chains of atoms. However, as long as $N \gg 1$, one can employ the boundary condition (2-52) also in the case of a linear chain. Imagine, for example, an infinite one-dimensional lattice divided into macroscopic sections of length $L = Na$. From the physical point of view, each section should have the same properties as a circular chain of length L , because as long as $N \gg 1$, each atom would "see" the same atomic configuration, the interaction between the atoms being confined to very small distances.

2-10. The equivalence of a vibrational mode and a harmonic oscillator

In Sec. 2-2 it was pointed out that the central problem of the specific heat of solids is the determination of the possible modes of vibration of the lattice under consideration. Once the answer to this question has been obtained, the vibrational energy of the solid is calculated on the assumption that the energy corresponding to a particular mode is the same as that of a harmonic oscillator of the same frequency. In the present section we shall show for the simple one-dimensional lattice of identical atoms that this identification is justified. For a general treatment of the three-dimensional case we refer to the literature.¹⁵

It is well known that the energy of a harmonic oscillator of mass M and angular frequency ω may be written

$$E = p^2/2M + M\omega^2 y^2/2$$

where y is the deflection and $p = M dy/dt$ is the momentum. In terms of y alone, we may write

$$E = \frac{1}{2}M(dy/dt)^2 + M\omega^2 y^2/2 \quad (2-57)$$

We shall now show that the energy associated with a vibrational mode can indeed be written in the form (2-57). Let us consider a mode corresponding to a standing wave $\sin qna \cos \omega t$. The kinetic energy of the particles in the lattice resulting from this vibrational mode is equal to

$$E_{\text{kin}} = \frac{1}{2}m \sum_n \left(\frac{dx_n}{dt} \right)^2 = \frac{1}{2}m\omega^2 \sin^2 \omega t \sum_n \sin^2 qna \quad (2-58)$$

¹⁵ M. Born and M. Goppert-Mayer, *Handbuch der Physik*, Vol. 24/2; see also F. Seitz, *Modern Theory of Solids*, McGraw-Hill, New York, 1940, p. 125.

where m is the mass per atom and the summation extends over all particles in the chain. The potential energy of the system due to the vibrational mode q is a function of all coordinates x_n ; let it be denoted by $V(x_0, x_1, \dots, x_n, \dots)$. The force exerted on particle n is then, in accordance with (2-42),

$$-\frac{\partial V}{\partial x_n} = m \frac{d^2 x_n}{dt^2} = f(x_{n-1} + x_{n+1} - 2x_n) \quad (2-59)$$

from this one may arrive at the following expression for the potential energy

$$V(x_0, x_1, \dots, x_n, \dots) = \frac{1}{2} f \sum_n (2x_n^2 - x_n x_{n+1} - x_n x_{n-1}) \quad (2-60)$$

(Note that each of the mixed terms appears twice in the summation, providing agreement between the last two equations; this may readily be verified by writing out the sum explicitly.) Substituting the standing wave solution into (2-60), one obtains after some manipulation,

$$V = 2f \sin^2(qa/2) \cos^2 \omega t \sum_n \sin^2 qna \quad (2-61)$$

Making use of the relation between ω and q as given by (2-44), one may write

$$V = \frac{1}{2} m \omega^2 \cos^2 \omega t \sum_n \sin^2 qna \quad (2-62)$$

The total vibrational energy resulting from mode q is obtained by adding (2-58) and (2-62), leading to

$$E = \frac{1}{2} m \omega^2 S \quad \text{with} \quad S = \sum_n \sin^2 qna \quad (2-63)$$

Note that this expression is independent of time. Suppose now we identify (2-62) with the potential energy of a harmonic oscillator, i.e., with the last term in (2-57). This requires evidently

$$y = (mS/M)^{1/2} \cos \omega t \quad (2-64)$$

If the vibrational mode were indeed equivalent with a harmonic oscillator, the kinetic energy should be, according to (2-57) and (2-64),

$$E_{\text{kin}} = \frac{1}{2} M (dy/dt)^2 = \frac{1}{2} m \omega^2 S \sin^2 \omega t$$

This expression is identical with (2-58), which proves the sought equivalence. The average energy associated with a particular mode of vibration of angular frequency ω_q is thus given by Planck's formula (2-14), i.e.,

$$\langle \epsilon \rangle = \frac{\hbar \omega_q}{e^{\hbar \omega_q / kT} - 1} \quad (2-65)$$

The number of quanta n_q associated with the vibrational mode of wave vector q at a temperature T is

$$n_q = \langle \epsilon \rangle / \hbar \omega_q = (e^{\hbar \omega_q / kT} - 1)^{-1} \quad (2-66)$$

The quanta are commonly referred to as phonons of frequency ω_q , in analogy with photons in the case of electromagnetic radiation. The concept of a phonon is convenient in the discussion of interaction of electrons with lattice vibrations in the theory of electrical conductivity. A phonon, like a photon, has particle aspects in the sense that one can associate with it a certain energy $\hbar \nu_q = \hbar \omega_q$ as well as a momentum $p = \hbar \nu_q / c_s$, where c_s is the velocity of propagation of the vibrational mode. Thus the "collision" between a phonon and an electron may be treated as a collision between two particles for which the conservation laws of energy and momentum hold.

2-11. The specific heat of a one-dimensional lattice of identical atoms

From the results obtained in the preceding sections it is a simple matter to derive an expression for the specific heat of a one-dimensional lattice of identical atoms. In the standing-wave representation the number of modes in the wave vector interval dq is, according to (2-56), equal to $L dq / \pi$ where L is the length of the chain. The wave vector is confined between 0 and π/a . The vibrational energy of the lattice at a temperature T is thus given by

$$E = \frac{L}{\pi} \int_0^{\pi/a} \frac{\hbar \omega_q}{\exp(\hbar \omega_q / kT) - 1} dq \quad (2-67)$$

where the summation over the possible wave vectors defined by (2-50) has been approximated by an integral. Employing the relation between ω_q and q as given by (2-44), one may replace dq by

$$\frac{dq}{d\omega} d\omega = \frac{2d\omega}{a\omega_{\text{max}} \cos(qa/2)} = \frac{2d\omega}{a(\omega_{\text{max}}^2 - \omega^2)^{1/2}} \quad (2-68)$$

Hence

$$E = \frac{2L}{\pi a} \int_0^{\omega_{\text{max}}} \frac{\hbar \omega d\omega}{[\exp(\hbar \omega / kT) - 1][\omega_{\text{max}}^2 - \omega^2]^{1/2}} \quad (2-69)$$

The specific heat as function of temperature may be obtained by differentiating with respect to T . The result is represented by the lower curve in Fig. 2-11 for a critical temperature $\theta = \hbar \omega_{\text{max}} / k = 200^\circ \text{K}$. It is of interest to compare this result with the continuum theory corresponding to the Debye approximation in one dimension. According to (2-24) the

number of vibrational modes in the range $d\omega$ of a continuous string of length L is equal to $L d\omega/\pi c_s$, where the velocity of propagation c_s is a constant. Applying this model to a string of atoms by a suitable cut-off of the frequency spectrum, one obtains for the vibrational energy

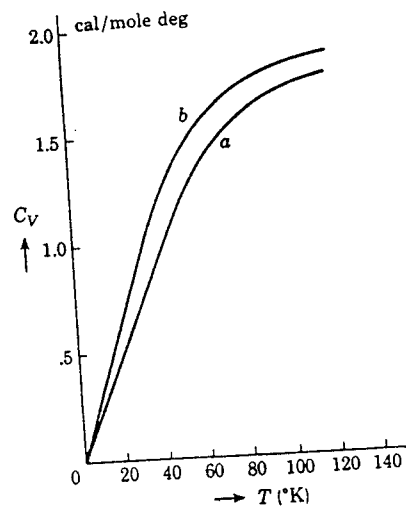


Fig. 2-11. Curve a represents the specific heat versus T for a monoatomic linear lattice according to (2-69); curve b refers to the Debye theory, representing C_V derived from (2-70). In both cases $\theta = 200^\circ\text{K}$. [After M. Blackman, *Proc. Roy. Soc., London, A148*, 365 (1935)]

$$E = \frac{L}{\pi c_s} \int_0^{\omega'_{\max}} \frac{\hbar \omega d\omega}{\exp(\hbar \omega/kT) - 1} \quad (2-70)$$

The upper limit ω'_{\max} in this case is determined by the fact that the number of modes is equal to the number of particles N in the string, i.e.,

$$\left(\frac{L}{\pi c_s} \right) \int_0^{\omega'_{\max}} d\omega = N \quad \text{or} \quad \omega'_{\max} = N\pi c_s/L \quad (2-71)$$

Note that this limit is different from that appearing in (2-69). The specific heat calculated on the basis of (2-70) is given by the upper curve in Fig. 2-11 again for a critical temperature $\theta = \hbar \omega'_{\max}/k = 200^\circ\text{K}$.

2-12. The vibrational modes of a diatomic linear lattice

Consider a diatomic lattice in one dimension as illustrated in Fig. 2-12; the distance between nearest neighbors will be denoted by a . The particles are numbered in such a way that the even numbers have a mass M , the odd ones m . In analogy with (2-42) we now have the following equations of motion, assuming nearest neighbor interaction only:

$$\begin{aligned} M\ddot{x}_{2n} &= f(x_{2n-1} + x_{2n+1} - 2x_{2n}) \\ m\ddot{x}_{2n+1} &= f(x_{2n} + x_{2n+2} - 2x_{2n+1}) \end{aligned} \quad (2-72)$$

We try to solve these equations by running waves of the type

$$x_{2n} = Ae^{-i(\omega t - 2nqa)} \quad \text{and} \quad x_{2n+1} = Be^{-i(\omega t - (2n+1)qa)} \quad (2-73)$$

where q is the wave vector of a particular mode of vibration; A and B

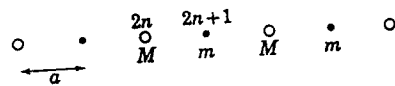


Fig. 2-12. A linear chain of equidistant masspoints M and m .

are the amplitudes corresponding to particles of mass M and m , respectively. Substitution of the solution into (2-72) yields the following two equations:

$$\begin{aligned} (M\omega^2 - 2f)A + 2Bf \cos qa &= 0 \\ (m\omega^2 - 2f)B + 2Af \cos qa &= 0 \end{aligned} \quad (2-74)$$

This system has nonvanishing solutions for A and B only if the determinant of the coefficients of A and B vanishes, i.e.,

$$\begin{vmatrix} (M\omega^2 - 2f) & 2f \cos qa \\ 2f \cos qa & (m\omega^2 - 2f) \end{vmatrix} = 0 \quad (2-75)$$

This gives for the square of the frequency the following two possibilities:

$$\omega^2 = f \left(\frac{1}{m} + \frac{1}{M} \right) \pm f \left[\left(\frac{1}{m} + \frac{1}{M} \right)^2 - \frac{4 \sin^2 qa}{Mm} \right]^{1/2} \quad (2-76)$$

Since ω should be positive, each value of ω^2 leads to a single value for ω . Thus in contrast to the monoatomic lattice, there are now two angular frequencies ω_+ and ω_- corresponding to a single value of the wave vector q . In a plot of ω versus q (Fig. 2-13) this leads to two "branches"; the one corresponding to ω_- is called the acoustical branch, the one associated with ω_+ is the optical branch. These two branches will now be discussed on the assumption that $M > m$. For $q = 0$ we obtain

$$\omega_+ = \left[2f \left(\frac{1}{m} + \frac{1}{M} \right) \right]^{1/2} \quad \text{and} \quad \omega_- = 0 \quad \text{for } q = 0 \quad (2-77)$$

From the form of (2-76) it is observed that here, as in the monatomic case, the frequency is a periodic function of the wave vector. The first zone thus limits the values of q to the range between $-\pi/2a$ and $+\pi/2a$ as shown in Fig. 2-13. For $q = \pm\pi/2a$, the two angular frequencies are evidently

$$\omega_+ = (2f/m)^{1/2} \quad \text{and} \quad \omega_- = (2f/M)^{1/2} \quad \text{for } q = \pm\pi/2a \quad (2-78)$$

The complete curves for ω_+ and ω_- versus q are illustrated in Fig. 2-13. The larger the mass ratio M/m , the wider the frequency gap between the two branches. The existence of a "forbidden" frequency (or energy)

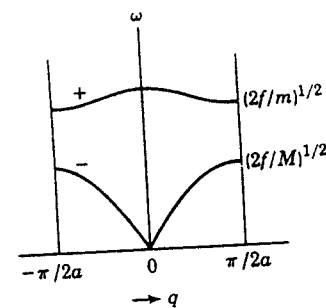


Fig. 2-13. The optical (upper curve) and acoustical (lower curve) branches corresponding to a diatomic linear lattice.

An investigation of NaCl has been made by Kellermann,¹⁸ using ionic and repulsive forces between the particles. Figure 2-16a gives the vibrational spectrum of NaCl obtained by Kellermann, and the difference with a continuum spectrum as used in the Debye theory is obvious. The Debye temperature θ_D as function of T calculated by Kellermann is given by the circles in Fig. 2-16b. It is observed that the theory is in remarkably good agreement with the curve obtained experimentally.

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PROBLEMS

2-1. (a) Give a derivation of expression (2-4) for the difference between C_p and C_V . (b) Calculate $C_p - C_V$ per mole of sodium at room temperature if at this temperature the compressibility of sodium is $12.3 \times 10^{-12} \text{ cm}^2 \text{ dyne}^{-1}$ and the linear coefficient of expansion is 6.22×10^{-5} ; compare the result with $C_p - C_V$ for a monatomic gas. Also calculate the Grüneisen constant for Na.

2-2. The possible energy levels of a rigid rotator according to quantum mechanics are given by $E_n = (\hbar^2/2J)n(n+1)$ where J is the moment of inertia and $n = 0, 1, 2, \dots$. For the molecules H_2 and Cl_2 calculate the energy difference between the ground state and the first excited state for rotation about an axis perpendicular to the line joining the nuclei. (Answers. Resp., 14.7×10^{-3} and $0.06 \times 10^{-3} \text{ ev.}$) Also estimate the value of $E_1 - E_0$ for rotation about the line joining the nuclei and show

¹⁸ E. W. Kellermann, *Phil. Trans.*, **A238**, 513 (1940); *Proc. Roy. Soc. (London)*, **A178**, 17 (1941).

that this rotation does not in general contribute to the rotational specific heat. At which temperatures for H_2 and Cl_2 do quantum effects enter in the rotational specific heat? If it is given that the number of possible states corresponding to an energy level E_n for a rotator is equal to $2n(n+1)$, show on the basis of statistical mechanics that the rotational specific heat for a molecule such as Cl_2 at room temperature is R cal per mole. (Hint: According to statistical mechanics the average energy at T is given by

$$\langle E \rangle = [\sum_n E_n Z_n \exp(-E_n/kT)] / [\sum_n Z_n \exp(-E_n/kT)]$$

where Z_n is the number of possible states associated with E_n . For the problem under consideration one can replace the summations by integrals.)

2-3. Discuss in some detail the specific heat of a diatomic molecule (including translation, rotation, and vibration). What is the value of C_p/C_V in various temperature regions?

2-4. Consider an array of N similar atoms, the separation between nearest neighbors being a . Discuss the specific heat of the system on the basis of the Debye approximation and show that at low temperatures the specific heat is proportional to T .

2-5. Discuss the specific heat of a two-dimensional square lattice with a nearest neighbor separation a on the basis of the Debye approximation. Show that at low temperatures the specific heat is proportional to T^2 .

2-6. Consider a cavity filled with black-body radiation in equilibrium with a temperature bath T . As is well known, the energy of radiation per unit volume u is a function only of T ; also, the radiation pressure $p = u/3$. In a p - V diagram, carry out a Carnot cycle with this "gas": first expand isothermally from V_1 to V_2 , then expand adiabatically such that the temperature drops slightly from $T - \Delta T$; finally, return to the starting point by isothermal and adiabatic compression. By making use of a well-known theorem about the efficiency of transforming heat into work, show that the energy density u is proportional to T^4 . Explain why the specific heat of the radiation gas is always proportional to T^3 , whereas for a solid in the Debye approximation this is true only at low temperatures.

2-7. Discuss in some detail the analogy between the mechanical properties of an array of equidistant similar atoms and a low-pass electric filter. (See, for example, Brillouin, *op. cit.*)

2-8. Discuss the specific heat of a solid on the basis of the cut-off procedure suggested by Born (Sec. 2-7) and show that one arrives at an expression of the type (2-41).

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chapter five

The Origin of the Quantum Theory

Relativity and quantum theory represent the two great conceptual remodelings of classical physics which were required to bring physics into the modern era. The quantum theory, first proposed by Planck in 1900, arose out of the inability of classical physics to explain the experimentally observed distribution of energy in the spectrum of a blackbody. By assuming that electromagnetic radiation was emitted by harmonic oscillators, the energy of which could change only by discrete energy jumps of amount $h\nu$, Planck was able to bring theory and experiment into accord. In the following 25 years striking confirmations of the quantum hypothesis came from several areas of physics.

5.1 Thermal Radiation

A hot body emits radiant energy, the quantity and quality of which depend on the temperature. Thus, the rate at which an incandescent filament

emits radiation increases rapidly with increase in temperature, and the continuous spectrum is formed. Such radiation is ordinarily emitted in an appreciable degree only by objects which are dense enough or thick enough to be opaque.

Radiation falling upon bodies is at least partially absorbed by them. At all temperatures bodies are emitting and absorbing thermal radiation; if they are neither rising nor falling in temperature, this is because as much radiant energy is absorbed each second as is emitted. In order to deal with the simplest possible case of thermal equilibrium, consider a cavity whose walls and contents are all at a common temperature. An isothermal enclosure of this sort is of special interest because the field of radiation inside it possesses some remarkably simple properties.

In an isothermal enclosure the stream of radiation in any given direction must be the same as in any other direction; it must be the same at every point inside the enclosure; and it must be the same in all enclosures at a given temperature, irrespective of the materials composing them. Furthermore, all these statements hold for each spectral component of the radiation taken separately.

Proof of these statements proceeds by showing that if any one of the statements were not true, a device could be constructed that would violate the second law of thermodynamics. For example, if the stream of radiation traveling west were greater than that traveling north, we could introduce two similar absorbers, one facing east and the other south. One of these absorbers would then become hotter than the other by absorbing radiant energy from the stronger stream. We could, therefore, operate a Carnot engine, using the two absorbers as source and sink, and so could convert heat continuously into work without causing other changes in the system, in violation of the second law. Radiation of a particular wavelength can be tested similarly by using selective absorbers.

The radiation field in an enclosure has important relations with the energy emitted by the walls or other physical bodies. An ideal black surface has the property that it absorbs completely all radiation falling upon it. Radiation leaving a black surface consists entirely of radiation emitted by it. Hence the stream of radiation emitted by any black surface or body in any direction is the same as the stream of radiation that travels in one direction in an isothermal enclosure at the same temperature. The total energy density produced just in front of a black surface by radiation emitted by that surface alone is just half as great as the density of energy in an enclosure at the same temperature, since the radiation emitted by the body is confined to a hemisphere of directions, whereas in the enclosure radiation is traveling in all directions.

Blackbody radiation is a phenomenon of great interest from the theoretical standpoint, because its properties have a universal character, being independent of the properties of any particular material substance. Several questions press at once for an answer. How does the energy density in blackbody radiation vary with the temperature? And what is the spectral distribution of the radiation? Furthermore, we wish to understand how this particular distribution is brought into existence by the atomic processes. Concerning the first two questions, it was found possible, during the last century, to obtain further information from thermodynamics without making any assumption as to the atomic process. The method consisted in considering the effect of expanding or contracting an isothermal enclosure and taking account of the work done on the walls by the radiation in consequence of radiation pressure. Appendix 5A summarizes many important classical developments in radiation theory.

5.2 Early Radiation Laws

In 1879 Stefan found empirically that the power emitted per unit area by a blackbody is proportional to the fourth power of the absolute temperature, or

$$R_b = \sigma T^4$$

where R_b = blackbody radiant emittance = power radiated per unit area
 σ = Stefan's constant = $0.5686 \times 10^{-7} \text{ W/m}^2 \cdot \text{K}^4$
 T = absolute temperature

Five years later Boltzmann deduced the Stefan-Boltzmann law, Eq. (5.1), from thermodynamical considerations (Sec. 5A.2).

Not only the quantity but also the quality of radiation emitted by a blackbody changes as the temperature increases. The distribution of energy in the blackbody spectrum is shown in Fig. 5.1. We define the monochromatic emissive power e_λ thus: the radiant power emitted per unit area in the spectral range λ to $\lambda + d\lambda$ is $e_\lambda d\lambda$; clearly, the radiant emittance $R = \int_0^\infty e_\lambda d\lambda$. From Fig. 5.1 one sees that e_λ is a function of both wavelength and temperature. In 1893 Wien showed (Sec. 5A.5) that for any blackbody

$$e_\lambda = T^5 f(\lambda/T) = \lambda^{-5} F(\lambda/T)$$

where $F(\lambda/T) = (\lambda T)^5 f(\lambda/T)$. Thus e_λ/T^5 is the same for all blackbodies,

as is shown in Fig. 5.2, where the data of Fig. 5.1, obtained in 1899 by Lummer and Pringsheim, are presented in a different form. A single curve serves to represent blackbody radiation at all temperatures. It follows that if λ_m is the wavelength at which e_λ is maximum,

$$\lambda_m T = \text{const} = 2.898 \times 10^{-3} \text{ m}^\circ\text{K} \quad (5.3)$$

for all temperatures—a special case of Wien's displacement law.

Thus, by reasoning based on thermodynamics, the problem of blackbody radiation is reduced to the determination of a single unknown function, $f(\lambda T)$ or $F(\lambda T)$. All attempts to obtain the correct form for this function from classical theory failed.

Two of the formulas proposed on a classical basis nevertheless

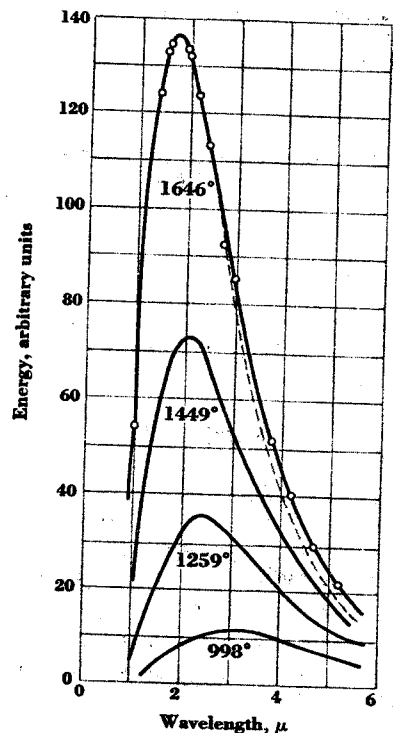


Fig. 5.1 Distribution of energy in constant wavelength interval $\Delta\lambda$ for the blackbody spectrum at four Kelvin temperatures.

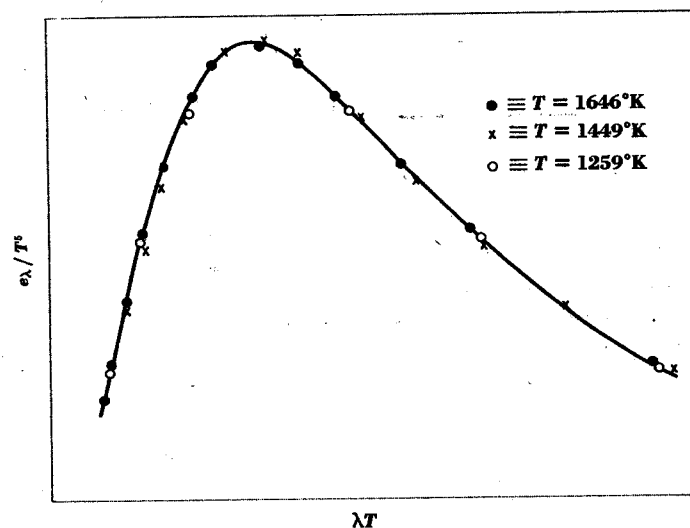


Fig. 5.2 Experimental verification of the Wien displacement law for blackbody radiation.

deserve mention. Wien derived a formula based on special assumptions regarding emission and absorption of radiation; he found that the energy density $U_\lambda d\lambda$ for wavelengths between λ and $\lambda + d\lambda$ is

$$U_\lambda d\lambda = \frac{1}{2} c e_\lambda d\lambda = C_1 \lambda^{-5} e^{-C_2/\lambda T} d\lambda \quad (5.4)$$

where c is the speed of light in free space. By proper choice of the undetermined constants C_1 and C_2 Wien's radiation law can be made to fit the data of Fig. 5.2 except at higher values of λT , where it predicts too low a value. In 1900 Rayleigh applied the principle of equipartition of energy to blackbody radiation. This led, with a contribution from Jeans, to a formula for e_λ which fitted the high- λT part of the e_λ curve but rose to infinity with decreasing λT . The reasoning employed by Rayleigh and Jeans, discussed below, has applications in modern physics.

5.3 Degrees of Freedom in an Enclosure

A typical vibrating system, such as a violin string or organ pipe, is capable of many modes of vibration. We are interested in the number of modes within a given frequency range for a cavity, but it is instructive

to apply the method first to a one-dimensional case. Let a string of great length L be stretched between two fixed points A and B . Standing waves can be set up only for those frequencies which give a whole number of loops between A and B . Since each loop corresponds to one-half a wavelength, standing waves occur only for those wavelengths λ for which

$$(5.5)$$

$$\left[\frac{L}{\lambda/2} = n_z = \frac{\lambda}{2L} \right]$$

where n_z is an integer.

We wish to know how many of these modes have wavelengths in the range between λ and $\lambda + \Delta\lambda$. If we decrease n_z by some integer Δn_z , the value of λ given by Eq. (5.5) increases to $\lambda + \Delta\lambda$, where

$$\frac{2L}{\lambda + \Delta\lambda} = n_z - \Delta n_z$$

When L is very great and $\Delta\lambda$ is small, we may write $\Delta n_z = -2L \Delta\lambda / \lambda^2$, where Δn_z now represents the number of modes of vibration with wavelengths in the range $\Delta\lambda$.

Now, associated with each mode there are two degrees of freedom, since the vibrations are transverse and any point on the string is free to move in a plane at right angles to the string. The total number of degrees of freedom per unit length of string in the wavelength range between λ and $\lambda + \Delta\lambda$ is therefore

$$(5.6) \quad \Delta n_l = \frac{\lambda}{4\Delta\lambda}$$

In two dimensions the situation is more complex but involves identical principles. Let us first discuss the system of waves in a square of side L (Fig. 5.3a). A set of waves moving initially in direction OM_1 will after reflection move in the direction M_1M_2 . After reflection at M_2 , the direction of propagation is M_2M_3 , which is parallel but opposite to OM_1 , etc. For this group of waves only four directions of motion are possible, $\neq OM_1$ and $\neq M_1M_2$. The four wave trains thus formed combine to produce a set of standing waves only if in both the x and y directions there is a whole number of half waves. Consider a cube of side L with perfectly reflecting walls in which there are electromagnetic waves polarized with the electric intensity in the z direction. Since the z component E_z of the electric intensity must be zero at the bounding planes when $x = 0$ or L and

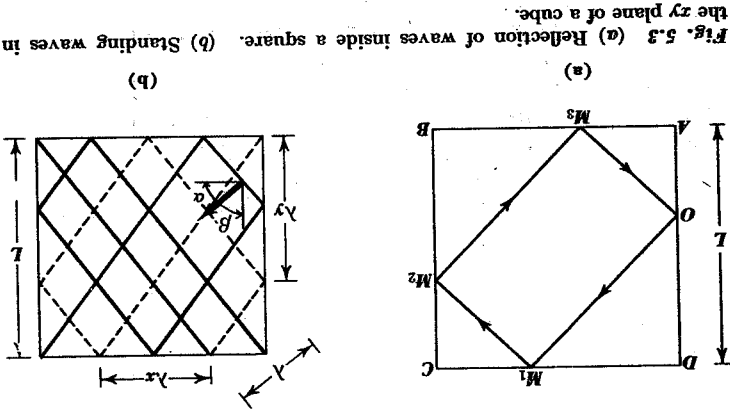


Fig. 5.3 (a) Reflection of waves inside a square. (b) Standing waves in the xy plane of a cube.

$y = 0$ or L , the allowed solutions of the wave equation are of the form

$$E_z = f(z, L) \sin \frac{n_x \pi}{L} x \sin \frac{n_y \pi}{L} y$$

where n_x and n_y are integers; this is the equation for a standing wave. The condition that there be nodes at the walls of Fig. 5.3b puts a limitation on the allowed wavelengths; specifically, the projection of any side along the propagation direction must be an integral number of half wavelengths. In Fig. 5.3b the heavy arrow represents one of the propagation directions, which makes angle $\alpha = 37^\circ$ with the x axis; for this particular case there are four half wavelengths associated with the x direction and three with y .

From the figure it is clear that $\lambda_x = L/\cos \alpha$ and

$$\lambda_y = \frac{\lambda}{\cos \beta} = \frac{\sin \alpha}{\lambda}$$

Since $\sin(n_x \pi x/L) = \sin(2\pi x/\lambda_x)$, we have $n_x \pi/L = (2\pi \cos \alpha)/\lambda$; similarly $n_y \pi/L = (2\pi \cos \beta)/\lambda$. If we solve for n_x and n_y , square each, and add, we have

$$\frac{4L^2}{\lambda^2} (n_x^2 + n_y^2) = \frac{4L^2}{\lambda^2} (\cos^2 \alpha + \cos^2 \beta) = \frac{\lambda^2}{\lambda^2} (\cos^2 \alpha + \sin^2 \alpha) = \frac{\lambda^2}{\lambda^2}$$

This method of constructing standing waves can be extended to a three-dimensional cube, for which eight sets of waves are involved. The condition $n_x \pi/L = (2\pi \cos \gamma)/\lambda$ must be applied, and since

$\cos^2 \alpha + \cos^2 \beta + \cos^2 \lambda = 1$, we find

$$n_x^2 + n_y^2 + n_z^2 = \frac{4L^2}{\lambda^2} \quad (5.7)$$

From this equation we can find the number of possible wavelengths which exceed a given value λ_m . This number is equal to the number of possible combinations of the positive integers n_x, n_y, n_z which make the left-hand member of Eq. (5.7a) less than $4L^2/\lambda_m^2$. To find this number, imagine each set n_x, n_y, n_z represented by a point on the three-dimensional plot of Fig. 5.4. These points lie at the corners of cubic cells of unit length. The number of values of n_x, n_y, n_z which give $\lambda > \lambda_m$ is therefore just the number of points inside a sphere of radius $2L/\lambda_m$ divided by 8 (since we are interested only in the all-positive octant), which is

$$n = \left(\frac{4\pi}{3} \frac{8L^3}{\lambda_m^3} \right) \frac{1}{8} = \frac{4\pi}{3\lambda^3} L^3$$

Differentiation of this equation gives the number of wavelengths in a range from λ to $\lambda + d\lambda$; thus

$$dn = \frac{4\pi d\lambda}{\lambda^4} (\text{vol of cube}) \quad (5.8)$$

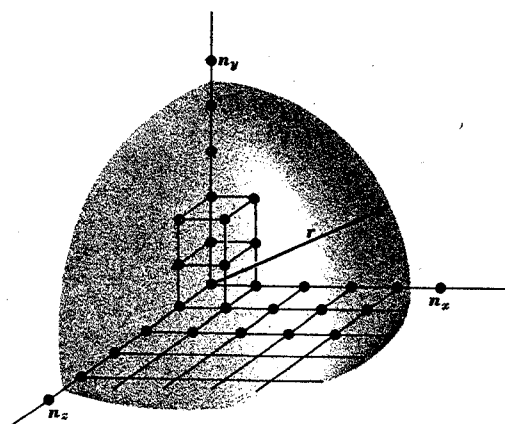


Fig. 5.4 The Rayleigh scheme for counting the number of allowed values of n_x, n_y, n_z for which $n_x^2 + n_y^2 + n_z^2$ is less than r^2 .

where both dn and $d\lambda$ are taken as positive for convenience. For electromagnetic waves there are two polarizations per allowed wavelength, and so we finally obtain for the number of degrees of freedom per unit volume for standing waves in the enclosure with wavelength from λ to $\lambda + d\lambda$ or frequency from ν to $\nu + d\nu$

$$g(\lambda) d\lambda = \frac{8\pi d\lambda}{\lambda^4} \quad g(\nu) d\nu = \frac{8\pi \nu^2 d\nu}{c^3} \quad (5.9)$$

5.4 The Rayleigh-Jeans Radiation Law

In an isothermal enclosure, the radiation is constant both in quantity and in spectral characteristics, so that any energy absorbed is reradiated. The result is the same as if all the energy were reflected at the walls. Rayleigh and Jeans assumed that oscillators in the wall absorbed and emitted radiation constantly, with each oscillator having its own characteristic frequency. For continuous operation of any given oscillator, standing waves must be set up in the enclosure. However for any enclosure of reasonable size the differences between neighboring frequencies are so small that the radiation appears to be continuous.

The principle of equipartition of energy requires assigning to these oscillators $\frac{1}{2}kT$ of kinetic energy per degree of freedom plus another $\frac{1}{2}kT$ for potential energy. Assignment of an average energy of kT to each mode of vibration leads to an energy density $U_\lambda d\lambda$ for waves with wavelength between λ and $\lambda + d\lambda$ given by

$$U_\lambda d\lambda = kTg(\lambda) d\lambda = 8\pi kT\lambda^{-4} d\lambda \quad (5.10)$$

Equation (5.10) is the Rayleigh-Jeans formula for blackbody radiation. It will be noted that it contains no new constants. At long wavelengths this formula agrees with observation, but near the maximum in the spectrum and at short wavelengths it gives much too large values. Furthermore, it assigns no maximum at all to U_λ . In fact, the energy density U in the enclosure would be infinite; for there is no lower limit to the possible wavelengths, and $U = \int_0^\infty U_\lambda d\lambda \rightarrow \infty$. In reality, the radiation density in an isothermal enclosure is ordinarily much less than the energy density due to thermal agitation of the molecules of a solid body; e.g., at 100°C U is about $7.5 \times 10^{-4} \text{ J/m}^3$, as compared with a total density on the order of 10^8 J/m^3 in iron. At temperatures above 10⁴°K the comparison would be reversed. Infinite energy in the electromagnetic field would make the specific heats of all material bodies infinite.

5.5 Planck's Investigation of Blackbody Radiation

The correct blackbody formula was discovered in 1900 by Max Planck. By introducing a radical innovation quite at variance with previous concepts, he found a formula in complete agreement with experiment. *This was the birth of the quantum theory.*

The experiments of Hertz on electromagnetic waves had seemed to give final confirmation to the electromagnetic theory of light, and this convinced Planck that the key to the blackbody spectrum would be found in the laws governing the absorption and emission of radiation by electric oscillators. We may imagine that the walls of an isothermal enclosure contain oscillators of all frequencies, essentially similar to the hertzian oscillator, and that the emission and absorption of radiation by the walls are caused by these oscillators.

Investigation by means of electromagnetic theory led Planck to the conclusion that an oscillator, in the long run, would affect only radiation of the same frequency as that of the oscillator itself. In the state of equilibrium, there would be a definite ratio between the density of radiation of any frequency ν and the average energy of the oscillators of that frequency. The problem of the blackbody spectrum was thus reduced to the problem of the average energy of an oscillator at a given temperature. If he then assumed the classical value kT for this average energy, as derived from the equipartition of energy, he was led to the Rayleigh-Jeans formula.

Planck, however, did not accept the principle of the equipartition of energy for oscillators. On the basis of a different assumption he was led at first to Wien's formula for the radiation density, Eq. (5.4). In 1900 new measurements of the blackbody spectrum by Lummer and Pringsheim and by Rubens and Kurlbaum showed definitely that Wien's formula is not correct. Planck discovered an empirical modification of Wien's formula that fitted the observations. Then he sought to modify the statistical theory of the distribution of energy among a set of oscillators so that the theory would lead to his new formula. He succeeded in doing so only after making a new assumption that broke drastically with classical principles. To facilitate understanding his assumption, a brief description of the statistical theory will be given.

5.6 Distribution of Energy among Oscillators in Thermal Equilibrium

Consider a linear oscillator of mass m that vibrates in simple harmonic motion; let its displacement be x and its momentum $p = m dx/dt$. The

potential energy of the oscillator can be written in the form $\frac{1}{2}bx^2$, b denoting the force constant; its kinetic energy is $\frac{1}{2}m(dx/dt)^2 = p^2/2m$. Thus its total energy is

$$\epsilon = \frac{p^2}{2m} + \frac{1}{2}bx^2 \quad (5.11)$$

and by elementary theory its frequency of vibration ν has the value

$$\nu = \frac{1}{2\pi} \sqrt{\frac{b}{m}} \quad (5.12)$$

When a large number of such oscillators are in thermal equilibrium, the energy of an individual oscillator varies widely but the energies of the entire group are distributed in energy according to the Maxwell-Boltzmann distribution (Sec. 4.6). By a contraction of Eq. (4.19) to two phase-space dimensions we find the number of oscillators dN with coordinates between x and $x + dx$ and momentum between p and $p + dp$ to be

$$dN = NAe^{-\epsilon/kT} dx dp \quad (5.13)$$

where A is a proportionality constant such that $\int dN = N$.

Since we are interested only in the energies of the oscillators, it is convenient to throw the formula into a different form. Let us construct a plot on which x and p are taken as cartesian coordinates (Fig. 5.5). Each oscillator is represented by a point on this plot which moves about as the oscillator vibrates. So long as the oscillator is free from disturbing forces, x and p change in such a way that the energy remains constant; hence the representative point moves along an ellipse given by Eq. (5.11) with a fixed value of ϵ . Throughout the elliptical ring between different energies ϵ and $\epsilon + \Delta\epsilon$, the quantity $e^{-\epsilon/kT}$ is sensibly constant; these ellipses, if $\Delta\epsilon$ is very small, the number of oscillators hence, in a state of thermal equilibrium, the number of oscillators represented by points in this ring is, by Eq. (5.13),

$$\Delta N = NAe^{-\epsilon/kT} \iint dx dp \quad (5.14)$$

The integral $\iint dx dp$ is the area of the elliptical ring, and its value is easily found in terms of $\Delta\epsilon$. We first note that the area inside an ellipse whose semiaxes are x_m and p_m is

$$S = \pi p_m x_m \quad (5.15)$$

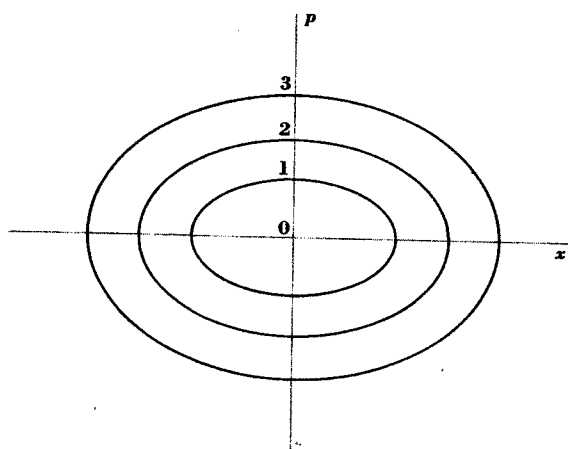


Fig. 5.5 The momentum-coordinate plane for a harmonic oscillator.

Here x_m and p_m also represent the maximum values of x and of p , respectively, during a vibration of an oscillator having an energy ϵ ; substituting in (5.11) first $x = x_m$ and $p = 0$ and then $x = 0$ and $p = p_m$, we find

$$x_m = \sqrt{\frac{2\epsilon}{b}} \quad p_m = \sqrt{2m\epsilon} \quad S = 2\pi\epsilon \sqrt{\frac{m}{b}} = \frac{\epsilon}{\nu} \quad (5.16)$$

by (5.12). The area of a ring corresponding to an increment $\Delta\epsilon$ is thus $\iint dx dp = \Delta S = \Delta\epsilon/\nu$. Hence (5.14) can be written in the form

$$\Delta N = NA_1 e^{-\epsilon/kT} \Delta\epsilon \quad (5.17)$$

where $A_1 = A/\nu$.

The average energy of the oscillators can now be found by summing their individual energies and dividing by N . Ordinarily this would be done by means of integrals, but for our present purpose we employ discrete sums. Let ellipses centered at the origin be drawn so as to divide the xp plane into rings of equal area h ; and let these rings, of which the innermost is actually an elliptical area, be numbered 0, 1, 2, ... from the center outward, as in Fig. 5.5. Then the total area inside ring number τ is $S = \tau h$; and, by Eq. (5.16), the energy of an oscillator represented by a point on the inner boundary of ring number τ is

$$\epsilon = S\nu = \tau h\nu$$

The number of oscillators N_τ on ring τ can thus be written, from (5.17),

$$N_\tau = N_0 e^{-\tau h\nu/kT}$$

where N_0 replaces $NA_1 \Delta\epsilon$. The total energy E of all oscillators is then, approximately,

$$E = \sum_0^\infty \tau h\nu N_\tau = N_0 h\nu e^{-h\nu/kT} (1 + 2e^{-h\nu/kT} + 3e^{-2h\nu/kT} + \dots) \\ = N_0 h\nu e^{-h\nu/kT} (1 - e^{-h\nu/kT})^{-2}$$

since by the binomial theorem the last series is of the form

$$1 + 2x + 3x^2 + \dots = (1 - x)^{-2}$$

In a similar way it is found that

$$N = \sum N_\tau = N_0 (1 + e^{-h\nu/kT} + \dots) = N_0 (1 - e^{-h\nu/kT})^{-1}$$

For the average energy per oscillator we have then, finally,

$$\bar{\epsilon} = \frac{E}{N} = \frac{h\nu}{e^{h\nu/kT} - 1} \quad (5.18)$$

This expression represents also the energy of a particular oscillator averaged over any length of time that is not too short. For, being similar, the oscillators will all have the same average energy in the long run, and this average must be E/N .

In classical theory it is now necessary to let $h \rightarrow 0$. The approximations made then disappear. Using the series $e^x = 1 + x + x^2/2 + \dots$, we find that, to the first order in h ,

$$e^{h\nu/kT} - 1 = \frac{h\nu}{kT}$$

Hence, in the limit as $h \rightarrow 0$, $\bar{\epsilon} = kT$. This is the same value for the average energy of a harmonic oscillator that was deduced from the equipartition of energy in Sec. 5.4, and it leads to the incorrect Rayleigh-Jeans formula.

5.7 Planck's Quantum Hypothesis

The new assumption introduced by Planck was equivalent to keeping h finite in the preceding formulas. In the first formulation of the new theory, Planck assumed that the oscillators associated with a given ring

all have the energy proper to the inner boundary of that ring. Then Eq. (5.18) for ϵ holds exactly. According to this assumption, the energy of an oscillator cannot vary continuously but must take on one of the discrete set of values $0, h\nu, 2h\nu, \dots, nh\nu$. The actual original form of Planck's assumption was that the energy of the oscillator must always be an integral multiple of a certain quantity ϵ_0 , but he then showed that for oscillators of different frequencies, ϵ_0 must be proportional to ν if the radiation law is to harmonize with the Wien displacement law. Thus he assumed that $\epsilon_0 = h\nu$, where h is a constant of proportionality. The connection between h and areas on the xp plane for the oscillator, as described above, was recognized by Planck later.

It must be emphasized that the assumption of a discrete set of possible energy values, or energy levels, for an oscillator was completely at variance with classical ideas. According to this assumption, if the energies of a large number of oscillators were measured, some might be found to have zero energy, some $h\nu$ each, others $2h\nu$, and so on. But not a single oscillator would be found which had energy, say, $1.73h\nu$. When the energy of a given oscillator changes, therefore, it must change suddenly and discontinuously. According to the older conceptions, the interchange of energy between two systems, e.g., between one gas molecule and another or between radiation and oscillators, is a continuous process, and the energy of an oscillator would likewise vary continuously. Such continuity of energy values is demanded by classical physics. For example, the electric and magnetic vectors in a light wave may have any values whatsoever, from zero up, and, accordingly, the wave may have any intensity, from zero up. The emission and absorption of this energy by the walls of an enclosure should, likewise, be a perfectly continuous process.

The problem of the absorption and emission of radiation presented serious difficulties for the new theory. If the energy of an oscillator can vary only discontinuously, the absorption and emission of radiation must be discontinuous processes. As long as the oscillator remains in one of its *quantum states*, as we now call them, with its energy equal to one of the allowed discrete values, it cannot be emitting or absorbing radiation according to the laws of classical physics, for then the conservation of energy would be violated. This is contrary to classical electromagnetic theory, which requires an isolated, accelerated electric charge to radiate energy. According to Planck's new theory, emission of radiation occurs only when the oscillator "jumps" from one energy level to another; if it jumps down to the next lower energy level, the energy $h\nu$ that it loses is emitted in the form of a short pulse of radiation. Absorption was also assumed at first to be discontinuous. An oscillator, Planck assumed, can absorb a

quantum $h\nu$ of radiant energy and jump up to its next higher energy level. This assumption met with special difficulties, however. For the classical wave theory, would spread out over an ever expanding wavefront, and it is hard to see how another oscillator could ever gather this energy together again so as to absorb it all and thereby acquire the energy for an upward quantum jump. Absorption ought, therefore, on Planck's theory, to be impossible.

To avoid this difficulty, Planck later modified his theory so as to allow the oscillators to absorb in a continuous manner, only the process of emission being discontinuous. The energy of an oscillator could then take on all values, as in classical theory, but every time the energy passed one of the critical values $nh\nu$, there was assumed to exist a certain chance that the oscillator would jump down to a lower energy level, emitting its excess energy as a quantum of radiation. This came to be known as the *second form* of Planck's quantum theory. It can be shown that in this form of the theory, the oscillators are evenly distributed over each ring on the xp plane, instead of being all on the inner boundary, and the mean energy of all oscillators is, instead of the value given by Eq. (5.18),

$$\bar{\epsilon} = \frac{h\nu}{e^{h\nu/kT} - 1} + \frac{1}{2}h\nu$$

(5.19)

Having read thus far, the student may perhaps have reached a state of confusion as to *what were* the essential assumptions of Planck's quantum theory! This confusion can be no worse than that which existed in the minds of most physicists in the year, say, 1911. The situation was made still more puzzling by the success of Einstein's theory of the photoelectric effect (Sec. 6.7); for Einstein assumed not only that radiation came in quantized spurts but that each spurt was closely concentrated in space, contrary to the wave theory. Confusion usually reigns while important physical advances are being made; it is only afterward that a clear-cut logical path can be laid down leading straight to the goal. One of the aims of this book will be to show how the theory gradually became clarified. It will be found that the following two new ideas introduced by Planck have been retained permanently and form a part of modern wave mechanics.

1. An oscillator or any similar physical system has a discrete set of possible energy values or levels; energies intermediate between these allowed values never occur.
2. The emission and absorption of radiation are associated with transitions, or jumps, between two of these levels; the energy hereby lost or gained by the oscillator being emitted or absorbed, respectively, as a quantum of radiant energy of magnitude $h\nu$, ν being the frequency of the radiation.

The difficulties with the theory of electromagnetic waves were overcome when the theory of wave mechanics was applied to the electromagnetic field itself.

It should be emphasized that Planck's revolutionary assumptions were not based upon an extension of the ordinary lines of reasoning of classical physics. Quite the contrary; they represented an *empirical modification* of classical ideas made in order to bring the theoretical deductions into harmony with experiment. Had the magnitude of the quantum of energy turned out to be not $h\nu$ but something *independent of the frequency*, the new theory might well have taken the form of a simple atomicity of energy, similar to the atomicity of electricity represented by the electronic charge. Such is not the case, however. Rather, it is the new universal constant h that represents the essentially new element introduced into physics by the quantum theory. We shall find h playing an important part in a wide variety of atomic phenomena.

5.8 Planck's Radiation Law

Planck derived his new radiation formula by considering the interaction between the radiation inside an isothermal enclosure and electric oscillators which he imagined to exist in the walls of the enclosure. A more direct and equally satisfactory procedure is to combine Planck's new expression for the mean energy of an oscillator with the analysis of the electromagnetic field by the method of Rayleigh and Jeans, in which the various modes of oscillation of the field inside an enclosure are treated as if they were oscillators. In Sec. 5.3, Eq. (5.9), we found that there would be $8\pi d\lambda/\lambda^4$ such modes of oscillation or degrees of freedom per unit volume in the wavelength range λ to $\lambda + d\lambda$. If we multiply this number by $\bar{\epsilon}$ as given by Eq. (5.18), we obtain

$$U_\lambda d\lambda = 8\pi \frac{d\lambda}{\lambda^4} \frac{h\nu}{e^{h\nu/kT} - 1}$$

Let us substitute here $\nu = c/\lambda$, c being the speed of light in vacuum. Thus we obtain, as Planck's new radiation law,

$$U_\lambda = \frac{8\pi ch}{\lambda^5} \frac{1}{e^{hc/\lambda kT} - 1} \quad (5.20)$$

[Strictly speaking, we should have used for $\bar{\epsilon}$ the value given by Eq. (5.19), which agrees with the value obtained from wave mechanics. The effect of this change would be to add in U_λ a term independent of tempera-

ture. Since only *changes* in U are perceptible, this term would be without physical effect.]

Planck's formula reduces to Wien's formula near one end of the spectrum and to the Rayleigh-Jeans formula near the other end. In Fig. 5.6 is shown a comparison between the several spectral-energy distribution formulas and the experimental data. The circles show observations by Coblentz on the energy distribution in the spectrum of a black-body at 1600°K. The reason that the curve for Planck's formula drops below the Rayleigh-Jeans formula is the failure of the classical principle of the equipartition of energy. The high-frequency modes of oscillation of the electromagnetic field in the enclosure, which should all have mean energy kT according to classical theory, remain almost entirely in their lowest quantum states and so contribute little to the observable density of radiant energy.

Planck's formula has the form that we found to be required by the principles of thermodynamics (Sec. 5.2); for Planck's formula can be

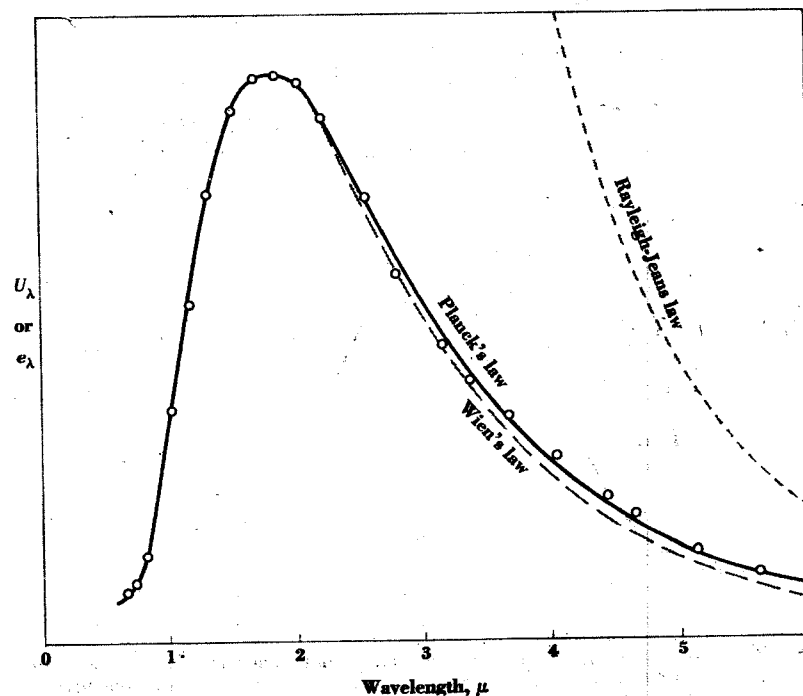


Fig. 5.6 Comparison of the three radiation laws with experiment at 1600°K.

written

$$U_\lambda = T^2 f(\lambda T) \quad f(\lambda T) = \frac{8\pi ch}{(\lambda T)^5} \frac{e^{ch/(\lambda T)} - 1}{1} \quad (5.20a)$$

From the formula in this form, both the Stefan-Boltzmann formula and the Wien displacement law follow as mathematical consequences. The value of the new constant h can be determined by comparing the observed values of U_λ with the formula, in which the values of all other quantities are known. In his original paper (1901) Planck obtained in this way the value $h = 6.55 \times 10^{-34}$. The accuracy of thermal data is relatively low, however, and better methods yield the value

$$h = 6.6256 \times 10^{-34} \text{ J-s}$$

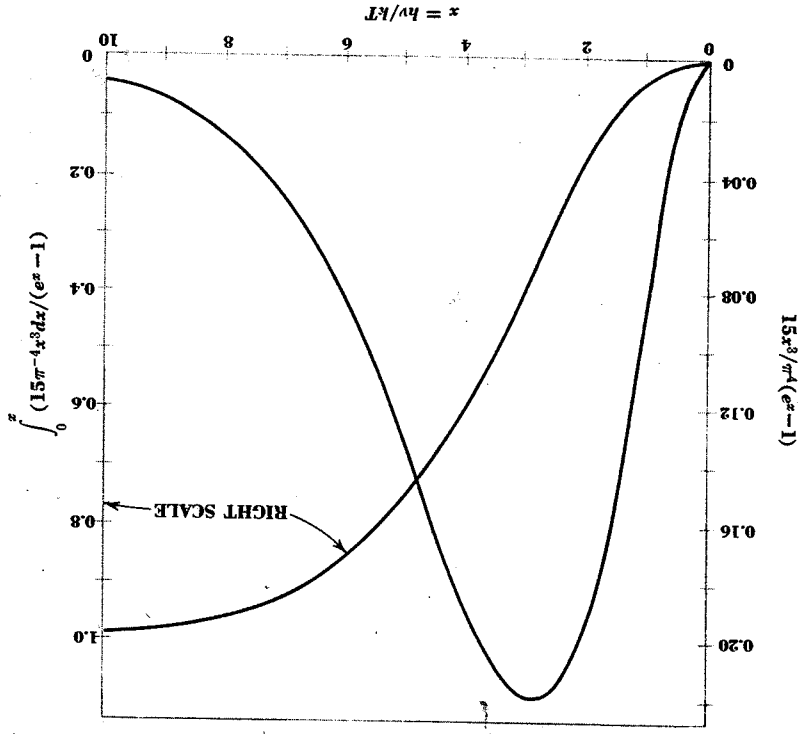


Fig. 5.7 Spectral distribution U_λ of blackbody radiation normalized to make U unity (left scale) and fraction of energy radiated with $x (= h\nu/kT)$ less than value given on abscissa (right scale).

It is often desirable to write the Planck law in terms of frequency rather than λ . In this case the energy density U_ν in the range between ν and $\nu + d\nu$ is

$$U_\nu d\nu = \frac{8\pi h \nu^3 d\nu}{c^3 (e^{h\nu/kT} - 1)} \quad (5.21)$$

$$\text{The total energy density } U \text{ is } U = \int_0^\infty U_\lambda d\lambda = \frac{8\pi k^4 T^4}{15 c^3 h^3} \int_0^\infty \frac{x^3 dx}{e^x - 1} = \frac{15 \pi^5 k^4 T^4}{30 \pi^5 c^3 h^3} \quad (5.22)$$

where $x = ch/\lambda kT$ and the integral has the value $\pi^4/15$. The normalized spectral distribution of a blackbody is shown in Fig. 5.7 along with a curve showing the fraction of the energy radiated at x less than a prescribed value. As is shown in Sec. 5A.1, Eqs. (5A.4) and (5A.5), the power radiated per unit area, total, or in a given λ or ν interval, is just $c/4$ times the appropriate energy density. Thus the power radiated per unit area is $R_B = cU/4$, and we have recovered Eq. (5.1) with the Stefan constant expressed in terms of π , k , c , and h .

Appendix 5A - Classical Radiation Theory

5A.1 Pressure and Energy Flux Due to Isotropic Radiation

Suppose a stream of radiation in a vacuum falls normally on the surface of a body. Then, if w is the mean energy density in the oncoming waves, they carry also w/c units of momentum per unit volume (Sec. 2.12). Thus the waves bring up to each unit area of the surface, along with cw J of energy, w units of momentum per second, the momentum as a vector being directed normally toward the surface. If the waves are absorbed by the surface, it receives this momentum and experiences, therefore, a pressure equal to w . Suppose, next, that the radiation is incident at an angle θ . Then the energy that crosses a unit area drawn perpendicular to the rays (PQ in Fig. 5A.1) is received by a larger area of magnitude $1/\cos \theta$ on the surface PR . Furthermore, the component of the momentum normal to the surface is less than in the case of normal incidence in proportion to $\cos \theta$. Thus the momentum in the direction of the normal that is delivered to unit area of the surface per second is decreased by the

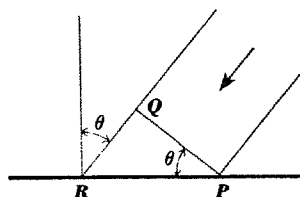


Fig. 5A.1

obliqueness of incidence in the ratio $\cos^2 \theta$, and the resulting pressure, if the radiation is entirely absorbed, is

$$p = w \cos^2 \theta$$

The same expression holds for the pressure caused by the emission of a beam at an angle θ or for the additional pressure caused by the occurrence of a reflected beam. If an incident beam is specularly reflected from a surface at the angle of incidence θ , the total pressure on the surface is $2w \cos^2 \theta$.

Finally, let radiation be streaming toward a surface and also away from it with equal intensities in all directions, as in an isothermal enclosure. Such a distribution of radiation is equivalent to a large number of beams of plane waves, all of equal intensity, with their directions of propagation distributed equally in direction. Let there be N beams in all, and let the energy density due to any one of them be w . Then the total energy density U just in front of the surface and the pressure p on it are, respectively,

$$U = Nw \quad (5A.1a)$$

$$p = \sum w \cos^2 \theta = w \sum \cos^2 \theta \quad (5A.1b)$$

To find this latter sum, imagine lines drawn outward from a point O on the surface to represent the various directions of the beams, whether moving toward the surface or away from it, and then about O as center draw a hemispherical surface of unit radius with its base on the surface (see Fig. 5A.2, where only two of the lines are shown). From the hemisphere cut out a ring-shaped element of area QS by means of two cones of semiangle θ and $\theta + d\theta$, drawn from O as apex and with the normal OP as axis. The edge of this element is a circle of perimeter $2\pi \sin \theta$, and its width is $d\theta$; hence its area is $2\pi \sin \theta d\theta$, whereas the area of the whole hemisphere is 2π . Now the lines of approach of the N beams of radiation, if drawn through O , will cut the hemisphere in points equally dis-

tributed over its surface. Hence, if we let dN denote the number of these lines that pass through the ring-shaped element, dN will be to N in the ratio of the area of the ring to the area of the hemisphere, so that

$$\frac{dN}{N} = \frac{2\pi \sin \theta d\theta}{2\pi} = \sin \theta d\theta$$

The value of $\cos^2 \theta$ is the same for all the dN beams. Hence their contribution to $\sum \cos^2 \theta$ is $\cos^2 \theta dN$ or, from the last equation, $N \cos^2 \theta \sin \theta d\theta$. Thus

$$\sum \cos^2 \theta = \int \cos^2 \theta dN = N \int_0^{\pi/2} \cos^2 \theta \sin \theta d\theta = \frac{1}{3}N \quad (5A.2)$$

(The limit is $\pi/2$ because directions all around the normal OP are included in the ring.) For the pressure we thus obtain, from Eq. (5A.1), $p = \frac{1}{3}wN$, or

$$p = \frac{1}{3}U \quad (5A.3)$$

Thus the pressure on the walls of an isothermal enclosure equals one-third of the radiant-energy density at any interior point.

It will be useful to calculate also the total energy brought up to the surface. Since half of the N waves are moving toward the surface and each wave delivers energy $cw \cos \theta$, the total energy brought up to unit area per second is

$$\frac{1}{2}N \int_0^{\pi/2} cw \cos \theta \sin \theta d\theta = \frac{1}{2}cwN = \frac{1}{2}cU$$

by (5A.1a). In an isothermal enclosure an equal amount of energy is carried away from the surface. It can be shown in the same way that in an isothermal enclosure in which the energy density is U , energy $\frac{1}{2}cU$ per second passes in each direction across unit area of any imaginary surface drawn inside the enclosure.

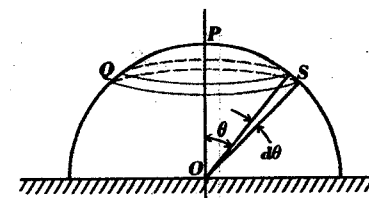


Fig. 5A.2

Furthermore, the energy emitted per second by unit area of any black surface, which is its radiant emittance R , is related to the energy density U in an isothermal enclosure having the same temperature by the equation

$$R = \frac{1}{4}cU \quad (5A.4)$$

The same relation holds for each wavelength separately. Let the energy emitted from the blackbody with a range of wavelengths $d\lambda$ be denoted by $e_\lambda d\lambda$ (so that $R = \int_0^\infty e_\lambda d\lambda$) and let the density of radiant energy in the enclosure within the same range of wavelengths be similarly represented by $U_\lambda d\lambda$ (so that $U = \int_0^\infty U_\lambda d\lambda$). Then

$$e_\lambda = \frac{1}{4}cU_\lambda \quad (5A.5)$$

5A.2 The Stefan-Boltzmann Law

In 1884, Boltzmann deduced a theoretical law for the variation of the total intensity of blackbody radiation with temperature. For this purpose, he applied the laws of the Carnot cycle to an engine in which the radiation played the part of the working substance.

The ideal Carnot engine consists of an evacuated cylinder with walls impervious to heat, a piston likewise impervious to heat and moving without friction, and a base through which heat may enter or leave. Let the walls, piston, and base be perfectly reflecting except for a small opening O in the base, which can be covered at will by a perfectly reflecting cover. Let this cylinder be placed with the opening O uncovered and opposite an opening in an evacuated isothermal enclosure B_1 , which is maintained at temperature T_1 (Fig. 5A.3). Then the cylinder will fill

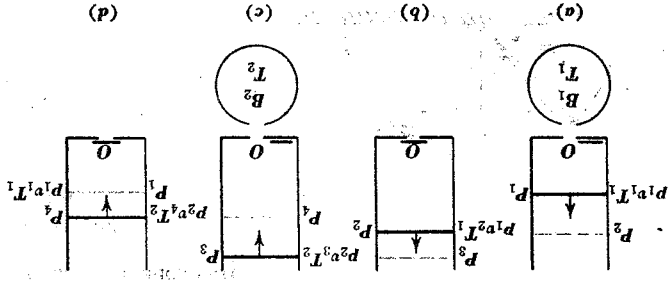


Fig. 5A.3 Boltzmann's radiation engine.

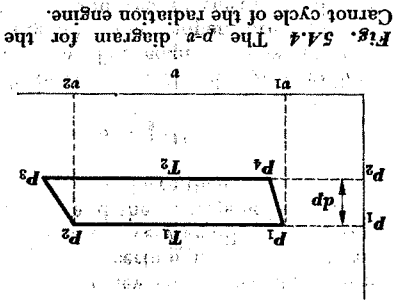


Fig. 5A.4 The p - v diagram for the Carnot cycle of the radiation engine.

up with radiation entering it through O from B_1 until there is the same density U_1 of radiation in the cylinder as there is in B_1 , at which time radiation will be passing at the same rate from O to B_1 as from B_1 to O . We may now consider the following cycle of events:

1. Starting with the piston in the initial position P_1 (Fig. 5A.3a), the initial volume of the cylinder being v_1 and the initial pressure due to the radiation $p_1 = \frac{1}{3}U_1$, we cause the piston to move upward, slowly, until position P_2 is reached, the volume increasing to v_2 . During this process the radiation density within the cylinder remains constant at U_1 . To keep it constant, additional radiation must enter the opening O from the enclosure B_1 , for two reasons:
 - a. Work W_1 is done by the radiation on the piston. If U_1 remains constant, so do U_1 and p_1 and

$$W_1 = p_1(v_2 - v_1) = \frac{1}{3}U_1(v_2 - v_1)$$

- b. The volume of the cylinder has increased by $v_2 - v_1$, which requires an additional influx of energy equal to $U_1(v_2 - v_1)$. Thus the total influx H_1 of radiation from B_1 must be

$$H_1 = \frac{1}{3}U_1(v_2 - v_1) + U_1(v_2 - v_1) \quad (5A.6)$$

This isothermal process is represented on the p - v diagram (Fig. 5A.4) by the horizontal line P_1P_2 . The energy H_1 is equivalent to heat supplied to the space within the cylinder, just as in an ordinary Carnot cycle the first isothermal expansion is accompanied by an absorption of heat. An amount of heat equal to H_1 must also be supplied from external sources to B_1 in order to keep the temperature of B_1 constant.

2. When the piston has reached P_2 , the perfectly reflecting cover is placed over the opening O (Fig. 5A.3b), thereby effecting complete thermal isolation of the interior of the cylinder, and a further expansion to position P_3 is made. External work is done, as before, on the piston, the energy required for this external work being supplied by the radiation. Partly because of this work and partly because of the increase in volume, the energy density of the radiation within the cylinder must decrease from U_1 to some smaller value U_2 . The pressure, likewise, has decreased. This is obviously an adiabatic process. It is represented in Fig. 5A.4 by the line P_2P_3 .

The new energy density U_2 is now equal to the energy density in an enclosure at a certain new temperature T_2 . If the expansion during this second process was very small, we may represent the change in temperature $T_1 - T_2$ by dT and the corresponding change in energy density $U_1 - U_2$ by dU . Since $p = \frac{1}{3}U$, we have then

$$dp = \frac{1}{3}dU \quad (5A.7)$$

dp representing the change in radiation pressure.

3. The engine is now placed opposite a second isothermal enclosure B_2 (Fig. 5A.3c) at temperature T_2 , the slide is removed from the opening O , and the piston is moved, by the application of suitable external force, from P_3 to P_4 . On account of this compression, there is a tendency for the density of radiation within the cylinder to rise and for radiation to pass through O into B_2 . The compression is supposed to take place so slowly, however, that the radiation density remains constant at a value only infinitesimally in excess of U_2 . During this second isothermal process, radiant energy in amount H_2 leaves the engine.

4. The piston having reached a suitable point P_4 , the opening O is closed, and the radiation is then compressed adiabatically until the initial position P_1 is reached.

The net external work done during this cycle is represented by the area $P_1P_2P_3P_4$ of Fig. 5A.4. If we assume the change of pressure to have been very small, this area equals $(v_2 - v_1) dp$. Calling the net external work dW , we have, therefore,

$$dW = (v_2 - v_1) dp = \frac{1}{3}(v_2 - v_1) dU$$

by (5A.7). Hence, by the usual rule for a Carnot cycle,

$$\frac{dW}{H_1} = \frac{T_1 - T_2}{T_1} = \frac{dT}{T_1}$$

and, using the value found for dW and also Eq. (5A.6), we have

$$\frac{dU}{U_1} = \frac{4dT}{T_1}$$

Thus, dropping the subscript,

$$\frac{dU}{U} = 4 \frac{dT}{T}$$

Integrated, this equation gives $\log U = 4 \log T + \text{const}$ or

$$U = aT^4 \quad (5A.8)$$

where a is a constant, not yet known. From Eq. (5A.4) we have then

also, for the emissive power or radiant emittance

$$R = \sigma T^4 \quad (5A.9a)$$

$$\sigma = \frac{1}{3}ca \quad (5A.9b)$$

Thus both the energy density of the radiation within an isothermal enclosure and the total emissive power of a blackbody are proportional to the fourth power of the absolute temperature T . This is the Stefan-Boltzmann law.

5A.3 Reflection from a Moving Mirror

In the preceding discussion no attention was paid to the spectral distribution of the radiation. The question presents itself, however, whether the same law can be applied also to the separate wavelengths. In order to investigate this question, we need to know what happens to the spectral distribution of a beam of radiation when it is reflected from a mirror that is in motion, such as the piston in the ideal apparatus that was described in the last section.

Let us consider first the effect of such motion upon a monochromatic beam. For this purpose we employ Huygens' principle. In Fig. 5A.5a, MM represents a mirror moving with a component of velocity V perpendicular to its plane. AB and DE represent parts of two incident waves which are one wavelength, or a distance λ , apart and are falling on the

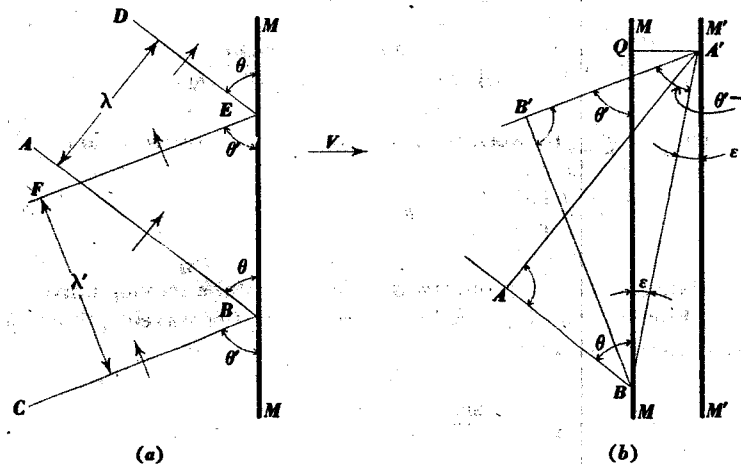


Fig. 5A.5 Reflection from a moving mirror.

mirror at an angle of incidence θ , CB and FE are parts of the same waves which have been reflected and are now leaving the mirror at an angle of reflection θ' , a distance λ' apart. It is obvious from the figure that $\lambda = BE \sin \theta$, $\lambda' = BE \sin \theta'$, whence

$$\frac{\lambda'}{\lambda} = \frac{\sin \theta}{\sin \theta'} \quad (5A.10)$$

To obtain a second relation between λ' and θ' , consider two successive positions of the same wave. In Fig. 5A.5b, the part AB of a wave is just beginning to fall on the mirror, whose instantaneous position is MM . The same portion of the wave at a later instant, after it has been reflected at the angle θ' , is shown by $A'B'$, the point A being now in contact at A' with the mirror, which is in the new position $M'M'$. While A traveled along the ray AA' , B traversed BB' ; hence $AA' = BB'$. The angles BAA' and $BB'A'$, being angles between ray and wave, are right angles. It follows, therefore, by similar triangles, that angle

$$B'A'B = ABA'$$

or

$$\theta' - \epsilon = \theta + \epsilon \quad (5A.11)$$

where ϵ is the angle QBA' . Furthermore, while A went from A to A' at the speed c of light, the mirror moved from MM to $M'M'$ at the speed u . Hence, if $A'Q$ is a perpendicular dropped from A' onto MM ,

$$\frac{c}{V} = \frac{AA'}{A'Q} = \frac{BA' \sin(\theta + \epsilon)}{\sin \epsilon} = \frac{\sin(\theta + \epsilon)}{\sin \epsilon} \quad (5A.12)$$

By eliminating ϵ between the last two equations, the equation

$$\tan \frac{1}{2}\theta' = \frac{c + V}{c - V} \tan \frac{1}{2}\theta \quad (5A.13)$$

is obtained, expressing the law of reflection from a moving mirror. Finally, from Eq. (5A.10), for the change of wavelength $\Delta\lambda$ caused by reflection, we find

$$\frac{\Delta\lambda}{\lambda} = \frac{\lambda' - \lambda}{\lambda} = \frac{\sin \theta'}{\sin \theta} - \sin \theta$$

We need the value of $\Delta\lambda$, however, only for an infinitesimal value of V

and hence of $\theta' - \theta$. For such a value

$$\sin \theta' - \sin \theta = (\theta' - \theta) \frac{d}{d\theta} \sin \theta = (\theta' - \theta) \cos \theta$$

Also, from Eqs. (5A.10) and (5A.11), in which ϵ is an infinitesimal,

$$\theta' - \theta = 2\epsilon = 2 \sin \epsilon = 2 \frac{c}{V} \sin(\theta + \epsilon)$$

to the first order; and here $\sin(\theta + \epsilon)$ may be replaced by $\sin \theta$. We thus find, to the first order in V ,

$$\Delta\lambda = 2 \frac{c}{V} \lambda \cos \theta \quad (5A.14)$$

5A.4 Effect of an Adiabatic Expansion upon Blackbody Radiation

Returning now to the sequence of operations described in Sec. 5A.2, let us consider the effect of the adiabatic process (step 2) upon the spectral distribution of the radiation. In this process, blackbody radiation initially at temperature T , imprisoned in a cylinder with perfectly reflecting walls is slowly expanded from an initial energy density U , to a new energy density U_2 . Let the former restriction to a small expansion be dropped. The change in direction of the rays that is produced by the moving piston, according to Eq. (5A.13), will tend to make the radiation no longer isotropic. We can obviate this inconvenient effect, however, by letting part of the walls of the cylinder reflect perfectly but diffusely. A surface of magnesium oxide does this very well. Then, if the expansion is made very slowly, because all rays (except a negligible few) strike the diffusing surface repeatedly, the radiation will be kept effectively isotropic; and the pressure on the piston, according to Eq. (5A.3), will be at all times equal to $\frac{1}{3}U$.

Let the cylinder have a cross section A and a (variable) length l . Then, if U is the energy density at any moment, when the piston moves outward a distance dl , work $p \, dl = \frac{1}{3}U A \, dl$ is done on it by the force due to radiation pressure. This work is done at the expense of the enclosed energy, the total amount of which is lAU . Hence

$$\frac{1}{3}U A \, dl = -d(lAU) = -AU \, dl - A l \, dU$$

$$\frac{dU}{U} = -\frac{4}{3} \frac{dl}{l}$$

and, after integration,

$$\log U = -\log l^3 + \text{const} \quad (5.15a)$$

$$U = Cl^{-3} \quad (5.15b)$$

C denoting a constant.

Now it can be shown by thermodynamic reasoning that an expansion of the type considered here cannot destroy the blackbody property of the radiation. For, at a certain instant, suppose that the expansion has reduced the total energy density to U_2 , and let T_2 be the temperature of an enclosure in which the density has this same value. Suppose that in the cylinder there were more radiation per unit volume of wavelengths near some value λ' than at the same wavelengths in the enclosure and less radiation near some other wavelength λ'' . It would then be possible to cause a little radiation to pass from the cylinder into a second enclosure at a temperature T'_2 slightly above T_2 by covering the opening in the base of the cylinder with a plate transmitting wavelengths near λ' but reflecting all others and putting the cylinder into communication with the second enclosure through this opening. In a similar way, enough radiation near λ'' could be passed into the cylinder from an enclosure at a slightly lower temperature T''_2 to restore the total energy to U_2 . Then the radiation could be compressed back to U_1 , the changes in U and l and the amount of the work done being just the reverse of these quantities during the expansion. Finally, putting the cylinder again into communication with the enclosure at T_1 , we could allow the spectral distribution to be restored to that proper to a blackbody at T_1 but without any net transfer of energy between cylinder and enclosure, since the total energy density has already been restored to that corresponding to T_1 . Thus we should have performed a cyclic operation, the only effect of which is to transfer heat energy from an enclosure at T'_2 to one at a higher temperature T''_1 . But this is inconsistent with the second law of thermodynamics.

Thus black radiation must remain black during any slow adiabatic expansion or compression. Its density and temperature, however, decrease. In the case under discussion, the last equation, in combination with Eq. (5A.8), gives

$$T \propto \frac{1}{l} \quad (5A.16)$$

To determine the effect on the spectral distribution, we must find the average rate at which wavelengths are increased. Suppose, first, that the walls of the cylinder and the piston reflect specularly. Then

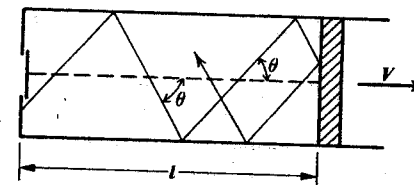


Fig. 5A.6

any ray preserves its angle of inclination to the axis of the cylinder θ in spite of repeated reflections (see Fig. 5A.6) and has, therefore, a constant component of velocity $c \cos \theta$ perpendicular to the piston. The ray strikes the piston $(c \cos \theta)/2l$ times a second, and its wavelength, according to (5A.14), increases each time by $(2V\lambda \cos \theta)/c$, V being the speed of the piston. Thus its wavelength increases at a rate

$$\frac{d\lambda}{dt} = \frac{c \cos \theta}{2l} \frac{2V\lambda \cos \theta}{c} = \frac{V\lambda}{l} \cos^2 \theta$$

If rays of wavelength λ are equally distributed in direction, the average value of $\cos^2 \theta$ for all of them is $\frac{1}{3}$, according to Eq. (5A.2); hence the average value of $d\lambda/dt$ for these rays is

$$\frac{d\lambda}{dt} = \frac{V\lambda}{3l} = \frac{\lambda}{3l} \frac{dl}{dt}$$

since $V = dl/dt$.

To simplify the calculation, suppose now that there is a diffusely reflecting spot on the walls. Then all the rays will take turns moving in the various directions, and all rays of wavelength λ will undergo the average change of wavelength just calculated. (This conclusion can be confirmed by a more complete analysis for which we have no space.) The last equation can be integrated thus:

$$\frac{d\lambda}{\lambda} = \frac{1}{3} \frac{dl}{l} \quad (5A.17a)$$

$$\log \lambda = \log l^{\frac{1}{3}} + \text{const} \quad (5A.17b)$$

$$\lambda \propto l^{\frac{1}{3}} \propto \frac{1}{T} \quad (5A.17c)$$

by (5A.16). Thus we have the conclusion that each spectral component of blackbody radiation must change in wavelength in such a way that $\lambda \propto 1/T$.

5A.5 The Wien Displacement Law

Now let us fix our attention on a particular spectral range from λ_1 to $\lambda_1 + d\lambda_1$, containing energy $U_{\lambda_1} d\lambda_1$ per unit volume in an enclosure at temperature T_1 . An adiabatic expansion which lowers the temperature to T_2 changes the limits of this range, according to the result just reached, to λ_2 and $\lambda_2 + d\lambda_2$, where

$$\lambda_2 = \lambda_1 + d\lambda_2 = \frac{\lambda_1}{T_1} + d\lambda_1 = \frac{\lambda_1}{T_2} \quad (5A.18a)$$

Therefore

$$\frac{d\lambda_2}{d\lambda_1} = \frac{T_1}{T_2} \quad (5A.18b)$$

The energy in $d\lambda_1$ is at the same time decreased, and in the same ratio as the total energy is; for in the argument that led up to Eq. (5A.15), we might have started with only the radiation in $d\lambda_1$ present in the cylinder. Hence, U_{λ_2} being the new value of U_{λ_1}

$$\frac{U_{\lambda_2} d\lambda_2}{U_{\lambda_1} d\lambda_1} = \frac{U_{\lambda_2}}{U_{\lambda_1}} = \frac{T_1^4}{T_2^4} \quad (5A.18c)$$

and using (5A.18b),

$$\frac{U_{\lambda_2}}{U_{\lambda_1}} = \frac{e_{\lambda_2}}{e_{\lambda_1}} = \frac{T_1^5}{T_2^5} \quad (5A.19)$$

Here e_{λ} is the emissive power of a blackbody, given in terms of U_{λ} by Eq. (5A.5).

Thus, if the values of U_{λ} or e_{λ} at two different temperatures are compared not at the same wavelength but at wavelengths inversely proportional to T , then their values will be found to be proportional to the fifth power of the absolute temperature. This conclusion is known as the *Wien displacement law*. It can also be expressed by saying that at a wavelength varied so that the product λT is held constant, U_{λ}/T^5 or e_{λ}/T^5 has the same value at all temperatures. Thus if either of these ratios is plotted against λT as abscissa, a single curve valid at all temperatures will be obtained (Fig. 5.2).

Problems

- 1 (a) Estimate the surface temperature of the sun, assuming it is essentially a blackbody of radius 7×10^8 m which is 1.5×10^{11} m from the earth, from the fact that the solar constant (power per unit area on a surface normal to the sun's rays) is 1400 W/m^2 .
(b) Estimate the surface temperature of the sun from the fact that $\lambda_m = 4900 \text{ \AA}$.
2. Show that Planck's radiation law, Eq. (5.20), reduces to Wien's law,

Eq. (5.4), when $h\nu \gg kT$ and to the Rayleigh-Jeans law, Eq. (5.10), when $h\nu \ll kT$.

3. If the fireball of a nuclear weapon can be approximated at some instant to be a blackbody of 0.5 m radius with a surface temperature of 10^7 K, find (a) the total electromagnetic power radiated, (b) the wavelength at which maximum energy is radiated, and (c) the value of kT in electron volts.

Ans: (a) $1.8 \times 10^{21} \text{ W}$; (b) 2.9 \AA ; (c) 0.86 keV .

4. From Fig. 5.7, assuming that the sun is a blackbody with $\lambda_m = 4900 \text{ \AA}$, estimate the fractions of the solar radiation in the visible (3500 to 7000 \AA), the infrared, and the ultraviolet parts of the spectrum.

Ans: 0.43, 0.50, 0.07

5. Show that if λ_m represents the wavelength at which maximum energy is radiated in wavelength interval $d\lambda$, then $\lambda_m T = ch/4.965k$, which is equivalent to Eq. (5.3).

6. A very bright star of spectral class B0 has an effective surface temperature of $20,000^\circ\text{K}$. Find the wavelength at which e_{λ} is maximum, assuming the radiation is approximately blackbody. How does e_{λ} at 5000 \AA for this star compare with that of the sun at this wavelength if the surface temperature of the sun is 6000°K ?

7. The intensity of radiation per unit wavelength interval from a fireball sphere of radius 2 m has been measured. When the resulting curve of intensity as a function of wavelength is plotted, it has its maximum at 289.8 \AA and is closely approximated by the blackbody curve. Find the temperature and the total power radiated by the sphere at the instant in question.

8. Show that the maximum of the U_{λ} curve (Fig. 5.7) in terms of $x = h\nu/kT$ occurs for $x = 2.82kT/h$.

9. Find the value of the Stefan constant σ in terms of k , c , and h by the use of Eq. (5.22).

Ans: $2\pi^5 k^4/15c^2 h^3$

10. Planck originally computed his value of h and the value of the Boltzmann constant k by using experimental results of Rubens and Kuribbaum, which gave $U = (7.6 \times 10^{-16} \text{ J/m}^2 \cdot \text{K}^4) T^4$ and

$$\lambda_m T = \frac{ch}{4.956k} = 2.9 \times 10^{-3} \text{ m} \cdot \text{K}$$

Find h and k from these data.

11. Estimate from Fig. 5.7 the fraction of the energy radiated by a blackbody which is in the visible region (3500 to 7000 \AA) for temperatures of 1000 , 2000 , and 3000°K .

RICHT 7

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CAP 7
- X RAYS



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chapter seven

X-rays

Probably no subject in all science illustrates better than x-rays the importance to the entire world of research in pure science. Within 3 months after Röntgen's fortuitous discovery, x-rays were being put to practical use in a hospital in Vienna in connection with surgical operations. The use of this new aid to surgery soon spread rapidly. Since Röntgen's time, x-rays have completely revolutionized certain phases of medical practice. However, had Röntgen deliberately set about to discover some means of assisting surgeons in reducing fractures, it is almost certain that he would never have been working with the evacuated tubes, induction coils, and the like, which led to his famous discovery.

In many other fields of applied science, both biological and physical, important uses have been found for x-rays. Transcending these uses in applied science are the applications of x-rays to such problems as the atomic and the molecular structure of matter and the mechanism of the interaction of

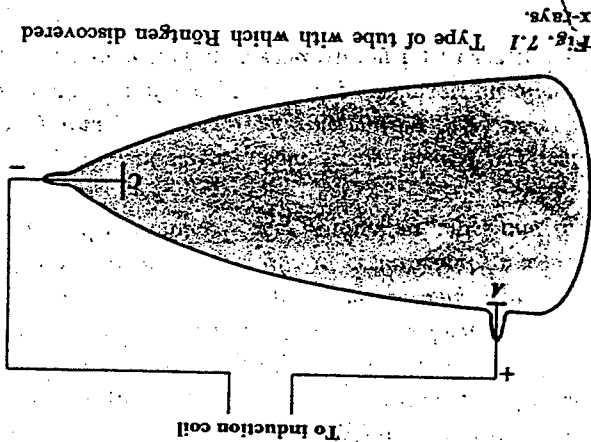
radiation with matter. X-rays provide us with a kind of supermicroscope, by means of which we can "see" not only atoms and their arrangement in crystals but also even the interior of the atom itself. Röntgen's discovery must be ranked among the most important.

7.1 The Discovery of X-rays

In the autumn of 1895, Wilhelm Konrad Röntgen, professor of physics at Würzburg, was studying the discharge of electricity through rarefied gases. A large induction coil was connected to a rather highly evacuated tube (Fig. 7.1), the cathode C being at one end and the anode A at the side. The tube was covered "with a somewhat closely fitting mantle of thin black cardboard." With the apparatus in a completely darkened room, he made the accidental observation that "a paper screen washed with barium-platino-cyanide lights up brilliantly and fluoresces equally well whether the treated side or the other be turned toward the discharge tube." The fluorescence was observable 2 m away from the apparatus. Röntgen soon convinced himself that the agency which caused the fluorescence originated at that point in the discharge tube where the glass walls were struck by the cathode rays.

Realizing the importance of his discovery, Röntgen at once proceeded to study the properties of these new rays—the unknown nature of which he indicated by calling them x-rays. In his first communications he recorded, among others, the following observations:

1. All substances are more or less transparent to x-rays. For example, wood 2 to 3 cm thick is very transparent. Aluminum 15 mm thick "weakens the



7.2 Production and Detection of X-rays

ment of a typical field of physics.

early work is beautifully illustrative of the qualitative phase of development of a typical field of physics.

It is a tribute to Röntgen's masterly thoroughness that most of the basic properties of x-rays were described in the paper first announcing the discovery. Intense interest was aroused, and work on x-rays began at once in many laboratories both in America and in Europe. This early work is beautifully illustrative of the qualitative phase of development of a typical field of physics.

1. Many other substances besides barium-platino-cyanide fluoresce—calcium compounds, uranium glass, rock salt, etc.
2. Photographs plates and films "show themselves susceptible to x-rays." Hence, photography provides a valuable method of studying the effects of x-rays.
3. X-rays are neither reflected nor refracted (so far as Röntgen could discover). Hence, "x-rays cannot be concentrated by lenses."
4. Unlike cathode rays, x-rays are not deflected by a magnetic field. They travel in straight lines, as Röntgen showed by means of pinhole photographs.
5. X-rays discharge electrified bodies, whether the electrification is positive or negative.
6. X-rays are generated when the cathode rays of the discharge tube strike any solid body. A heavier element, such as platinum, however, is much more efficient as a generator of x-rays than a lighter element, such as aluminum.

effect considerably, though it does not entirely destroy the fluorescence." Lead glass is quite opaque, but other glass of the same thickness is much more transparent. "If the hand is held between the discharge tube and the screen the dark shadow of the bones is visible within the slightly dark shadow of the hand."

Until 1913, tubes for the production of x-rays were similar to a form suggested by Röntgen. A residual gas pressure of the order of 10^{-7} mm Hg provides, when voltage is applied, a few electrons and positive ions. These positive ions, bombarding the cathode, release electrons, which, hurried against the anode, give rise to x-rays. A curved cathode converges the electrons into a focal spot of desired shape and size. In this type of tube, known as the *gas tube*, the anode current, applied voltage, and gas pressure are more or less independent, and it is essential that the gas pressure be maintained at the desired value. Various ingenious devices were introduced for accomplishing this. In 1913, however, an important improvement was introduced by Coolidge. He evacuated the filament of tungsten to serve as a source of electrons. The filament was heated by an adjustable current from a battery. Thus the electron current could be controlled independently of the applied voltage.

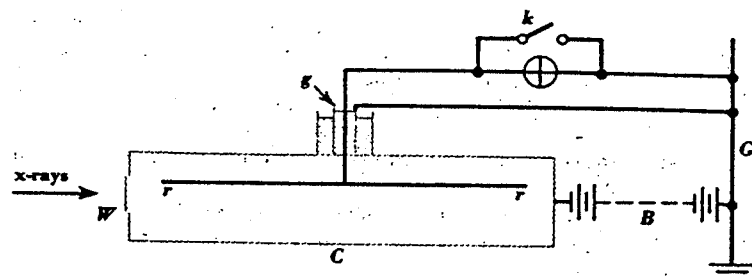


Fig. 7.2 An ionization chamber for measuring the intensity of a beam of x-rays or other ionizing radiation.

For quantitative measurements, the ionization method was early adopted. The discharging effect of x-rays upon charged bodies was traced to ionization of the molecules of the surrounding gas. The effect was found to increase rapidly with density and also to depend on the nature of the gas, the following being increasingly active in the order: H_2 , CO , air, CO_2 , ether vapor, CS_2 . At first the rate of discharge of an electroscope was used in measuring the intensity of an x-ray beam, but later an *ionization chamber* was introduced. This is shown schematically in Fig. 7.2. C is a metal tube several centimeters in diameter, from about 20 to 100 cm long, and closed at both ends except for an opening or window W , over which may be placed a thin sheet of cellophane or aluminum for admitting the x-rays. A rod rr suitably supported by good insulating material, such as amber or quartz, is connected to an electrometer or a vacuum-tube amplifier. An electric field is maintained between the rod rr and the cylinder C by a battery B . The chamber may be filled with a heavy gas to make the arrangement more sensitive; argon or methyl bromide is often used. When x-rays enter the window W , the gas within the cylinder is made conducting, and because of the electric field between the cylinder and the rod, the latter acquires a charge at a rate which is a measure of the intensity of the x-ray beam. Nowadays a Geiger counter or a scintillation detector with appropriate electronic circuits may replace the ionization chamber.

7.3 Wavelengths of X-rays

Although the hypothesis that x-rays are a form of electromagnetic radiation was early suggested, it proved to be difficult to establish. Evidence for the *diffraction* of x-rays was reported in 1899 by Haga and Wind, who concluded that the wavelengths of x-rays must be of the order of

10^{-10} m, but their experiments were regarded by many as inconclusive. They used wedge-shaped slits only a few microns wide and observed a slight broadening of the image on a photographic plate. The first practical method for resolving x-ray beams according to wavelength developed out of a brilliant suggestion by Laue. The order of magnitude of x-ray wavelengths, as revealed by the diffraction experiment described above, is the same as the order of magnitude of the spacing of the atoms in crystals. Laue suggested, therefore, that a crystal, with its regular array of atoms, might behave toward a beam of x-rays in somewhat the same way as a ruled diffraction grating behaves toward a beam of ordinary light. Assume that plane electromagnetic waves traveling in a given direction fall upon a crystal. Each atom scatters some of the incident radiation. The wavelets scattered by different atoms combine, in general, in all sorts of phases and so destroy each other by interference. Laue argued, however, that for certain wavelengths and in certain directions the wavelets should combine in phase and so produce a strong diffracted beam. It would be expected, therefore, that such diffracted beams might be observed upon passing a heterogeneous x-ray beam through a crystal.

Such an experiment was performed by Friedrich and Knipping in 1912. A narrow pencil of x-rays was allowed to pass through a crystal beyond which was a photographic plate. After an exposure of many hours, it was found on developing the plate that, in addition to the interior central image where the direct beam struck the plate, there were

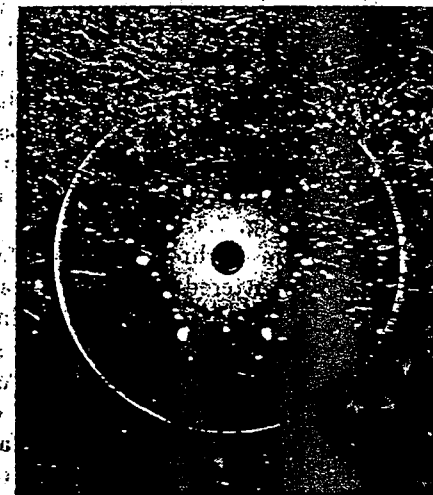


Fig. 7.3 Laue photograph of a tungsten crystal.

present on the plate many fainter but regularly arranged spots, indicating that the incident x-ray beam had been diffracted by the crystal in certain special directions, just as Laue had predicted (Fig. 7.3). In their original paper, Friedrich, Knipping, and Laue, from an analysis of a series of photographs of a crystal of zinc blende oriented at various angles with respect to the incident pencil, concluded that there were present in the x-ray beam wavelengths varying between 1.27 and 4.83×10^{-11} m. This result supported the two postulates underlying the experiment: (1) that x-rays are electromagnetic waves of definite wavelengths, and (2) that the atoms of a crystal are arranged in regular three-dimensional order, as suggested by the external symmetry of crystals.

This experiment marked the beginning of a new era in x-rays. Two new fields of investigation were at once opened up: (1) in x-rays, the study of spectra and the use of homogeneous beams in experiments on scattering, absorption, etc.; (2) the study of the arrangements of atoms or molecules in crystals. In the following sections, we shall confine our discussion to some of the more important aspects of the former field.

7.4 Bragg's Law

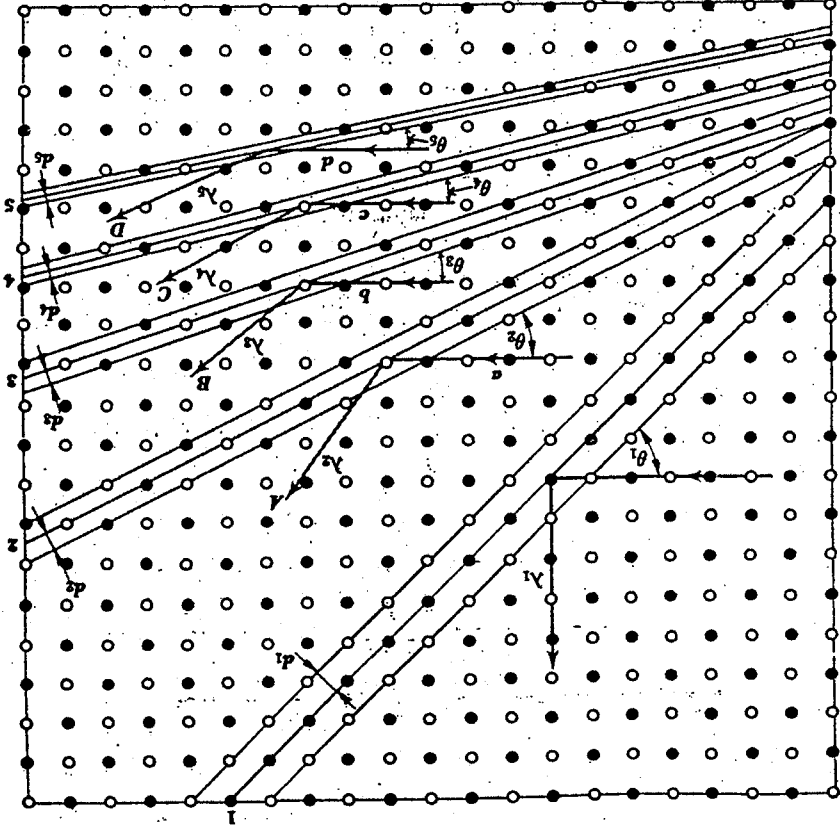
Immediately following the announcement by Friedrich, Knipping, and Laue of their successful experiment many investigators took up the study of the new phenomenon. A simple way of looking at the process of diffraction by a crystal grating was proposed by W. L. Bragg. He pointed out that through any crystal a set of equidistant parallel planes can be drawn which, among them, pass through *all* the atoms of the crystal. Indeed, a great many such families of planes can be drawn, the planes of each family being separated from each other by a characteristic distance. Such planes are called *Bragg planes*, and their separations, *Bragg spacings*. Traces of five families of Bragg planes are shown in Fig. 7.4.

If plane monochromatic waves fall upon the atoms in a Bragg plane, a wavelet of scattered radiation spreads out from each atom in all directions. There is just one direction in which, irrespective of the atomic distribution in the plane, the scattered wavelets meet in the same phase and constructively interfere with each other, viz., the direction of specular reflection from the plane for which there is no path difference for radiation scattered by atoms in the plane. This follows from the ordinary Huygens construction as used for the reflection from a mirror. The

For a regular array of atoms in one plane there are also other directions for which constructive interference could occur, but for these directions there is destructive interference of the wavelets from the set of parallel planes.

beam scattered in this direction may be thought of as "reflected" from the Bragg plane. But each Bragg plane is one of many regularly spaced, parallel planes; the beams reflected from these various parallel planes combine, in general, in different phases and so destroy each other by interference. Only if certain conditions of wavelength and angle of incidence of the beam on the planes are satisfied do the waves from different planes combine in the same phase and reinforce each other. In Fig. 7.5 the horizontal lines represent the traces of two successive Bragg planes spaced d apart. Consider a plane wave incident on these planes with θ the angle between the propagation direction of the incident beam and the planes; θ is known as the *glancing angle*, and the reflection condition requires that $\theta = \theta'$. For radiation scattered by the second plane to

Fig. 7.4 Reflection of monochromat-
heterochromatic radiation is incident.



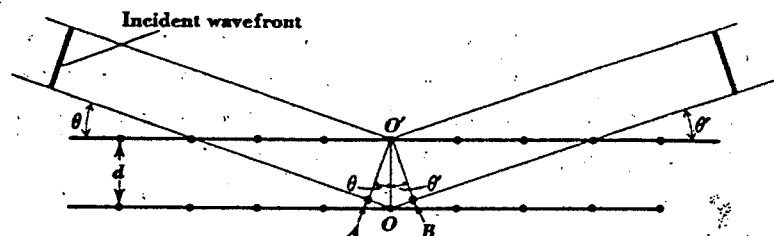


Fig. 7.5 Constructive interference of the waves scattered from atoms of a crystal occurs when $n\lambda = 2d \sin \theta$.

interfere constructively with that scattered by the first, the path difference AOB must be an integer number of wavelengths, whence

$$n\lambda = 2d \sin \theta \quad (7.1)$$

where n is an integer called the *order of the reflection*. Equation (7.1) together with the requirement that $\theta = \theta'$ constitutes *Bragg's law* for x-ray "reflection."

Suppose, now, that a parallel wave train containing a *continuous spectrum* of wavelengths is incident upon a crystal, as represented by the parallel arrows a, b, c, d in Fig. 7.4. In the figure, traces of five families of Bragg planes are shown, numbered 1, 2, 3, 4, 5, with their characteristic spacings d_1, d_2, \dots . Many other families of planes might be imagined, some perpendicular and some not perpendicular to the plane of the paper. Suppose that in the incident beam there is a wavelength λ_2 such that $n\lambda_2 = 2d_2 \sin \theta_2$, where n is an integer, d_2 is the distance between the set of planes numbered 2, and θ_2 is the glancing angle between the direction of the incident radiation and these planes. Then there will be reflected from this group of planes a beam A , of wavelength λ_2 , which will proceed in the direction of the arrow A . Similarly, we may have reflected beams B, C, D, \dots in different directions in the plane of the paper, and also many other beams reflected from other families of planes in directions not in the plane of the paper. Each *Laue spot* in the experiment of Friedrich and Knipping may be interpreted as produced by such a reflected beam. In general, the most intense spots correspond to reflections from Bragg planes containing the greatest number of atoms on each plane.

7.5 The X-ray Spectrometer

W. H. Bragg and his son W. L. Bragg were responsible for the early

from target T pass through two narrow slits S_1 and S_2 and fall at glancing angle θ on the cleavage face of a crystal K —rock salt, calcite, mica, gypsum, quartz, etc.—mounted on a table D , the angular position of which can be read. The reflected beam, which makes an angle 2θ with the incident beam, enters an ionization chamber C by means of which the intensity can be measured.

For photographic registration, the ionization chamber can be replaced by a photographic plate PP (Fig. 7.6b). With the crystal set at a glancing angle θ , the reflected beam will strike the plate at L (or at L' , if the crystal is reversed). From the position O at which the direct beam strikes the plate, the distances OL and OA , and hence the angle 2θ , can be determined.

The distance d between the reflecting planes of a crystal such as NaCl is determined as follows. In the rock-salt crystal, Na and Cl ions occupy alternate positions in a cubic lattice similar to that in Fig. 7.4, which represents one plane of atoms. Taking the atomic weight of Cl as 35.45 and of Na as 22.99, we find the molecular weight of NaCl to be 58.44. Therefore, 58.4 kg of the NaCl contains $2N_A$ atoms, where N_A is Avogadro's number. Thus we find for the number of atoms n in

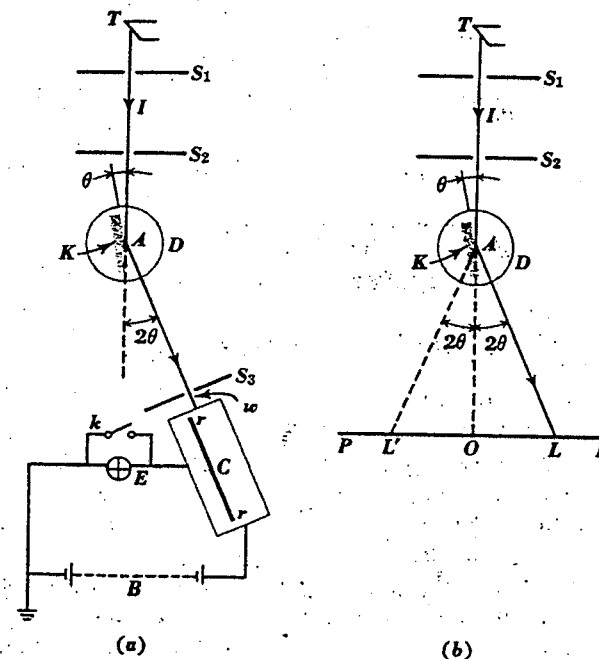


Fig. 7.6 An x-ray spectrometer using (a) ionization detector.

1 m³ of rock salt $2N_{Ap}/58.44$, where $\rho = 2164$ kg/m³, the density of crystalline NaCl. If d is the distance between the center of one atom and the next along the edge of the cube, $1/d$ is the number of atoms in a row of atoms 1 m long, and $n = 1/d^3$. From these two equations $d = 2.82 \times 10^{-10}$ m = 2.82 Å.

By using crystal gratings, x-ray wavelengths can be compared with a precision of a few parts in 10⁶, which is more precise than Avogadro's number and the density and molecular weight of a typical crystal are known. Therefore, x-ray wavelengths have often been reported in terms of X units, defined by taking the grating space of calcite at 18°C to be 3029.45 XU. It is now known that the X unit is 0.0202 percent less than 10⁻¹⁰ m. Table 7.1 lists some crystals commonly used in x-ray spectroscopy together with their grating spaces and the linear expansion per degree Celsius.

Table 7-1. Grating spaces of some crystals used in x-ray spectroscopy

Crystal	Grating Space d at 18°C		Change in d per Degree Celsius, XU or 10 ⁻¹⁰ m	Rock salt, NaCl Calcite, CaCO ₃ Quartz, SiO ₂ Gypsum, CaSO ₄ ·2H ₂ O Mica
	Corrected, XU	× 10 ⁻¹⁰ m		
	2814.00	2819.68	0.11	
	3029.45	3035.57	0.03	
	4246.02	4254.60	0.04	
	7584.70	7600.0	0.29	
	9942.72	9962.8	0.15	

With a beam of x-rays from a platinum target incident on the cleavage face of a rock-salt crystal, W. H. Bragg rotated the crystal in steps of $\Delta\theta$ and the ionization chamber in steps of $2\Delta\theta$. He plotted the curve of ionization current against glancing angle θ and found that the x-ray intensity did not vary uniformly with angle but rose at certain angles to a sharp maximum. A curve similar to that shown in Fig. 7.7 was obtained. A group of three maxima, a_1 , b_1 , and c_1 , was observed at the respective angles θ of 9.9, 11.6, and 13.6°. A second group of three maxima, a_2 , b_2 , and c_2 , was observed at approximately double these angles. Bragg interpreted the maxima a_1 , b_1 , and c_1 as second-order angles.

7.6 Monochromatic Characteristic Radiation

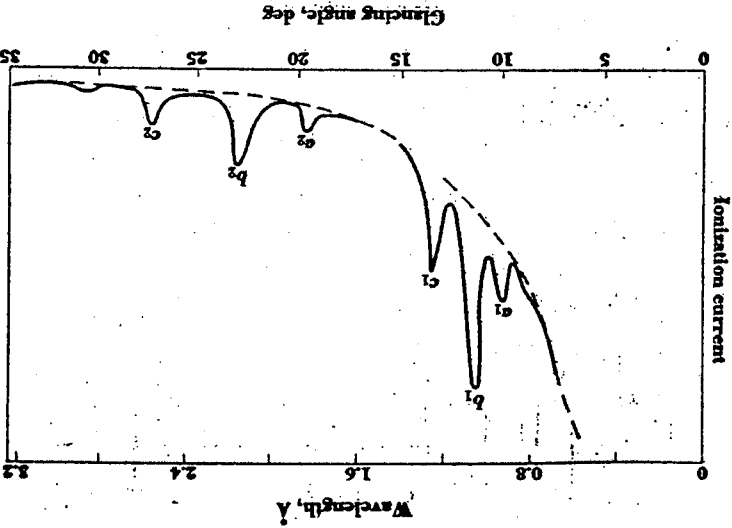


Fig. 7.7 Bragg's curve for the energy distribution in an x-ray spectrum, showing the characteristic lines a_1 , b_1 , c_1 .

reflections of the lines a_1 , b_1 , and c_1 . He computed their wavelengths, taking $n = 1$ for the lines a_1 , b_1 , and c_1 and $n = 2$ for the second-order lines a_2 , b_2 , and c_2 , and obtained 0.97, 1.13, 1.32 Å, respectively.

Curves similar to Fig. 7.7 were obtained with other crystals, the only difference being that the maxima occurred at different glancing angles, indicating that each crystal had a characteristic grating space d . Bragg convinced himself, however, that these respective maxima for different crystals always represented the same monochromatic radiation, since, for example, the absorption in aluminum of peak b_1 was always the same, whatever the crystal used. In short, the peaks of the curve in Fig. 7.7 represent spectral lines the wavelengths of which are characteristic of the target emitting the rays. These monochromatic lines are superimposed on a continuous spectrum represented by the partially dotted line in the figure. Curves of the type shown in Fig. 7.7, therefore, represent the distribution of energy in the x-ray spectrum, continuous and characteristic combined, of an element.

The development of the Bragg spectrometer made it possible to make precise measurements of x-ray wavelengths. In 1913 Moseley undertook a systematic study of x-ray spectra emitted by targets of a number of elements of medium and high atomic number. His results were soon supplemented by data from other observers. X-ray spectra of a number of different elements are shown in Fig. 7.8. For each ele-

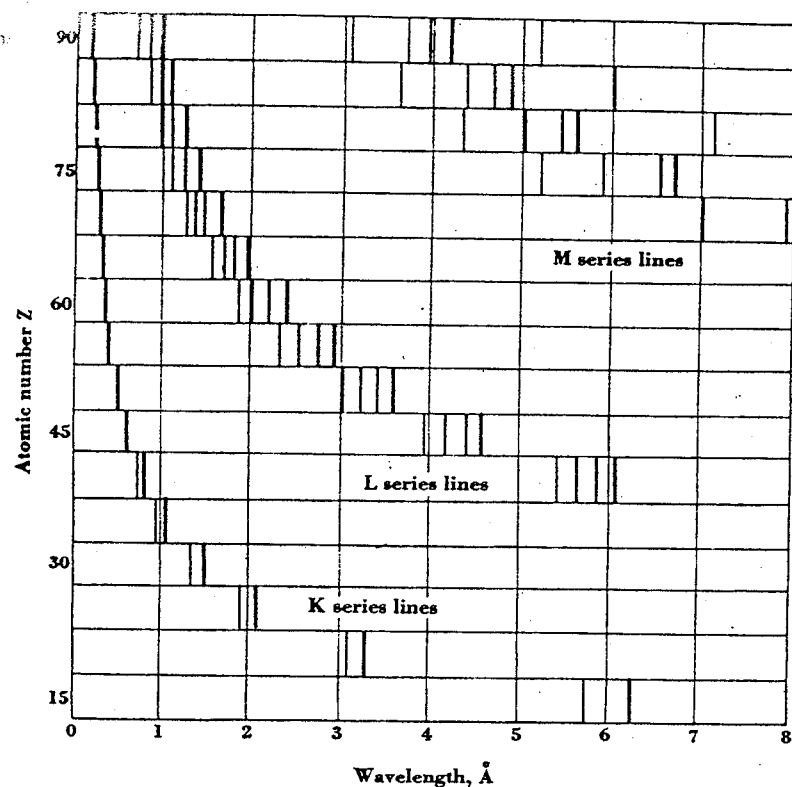


Fig. 7.8 Wavelengths of some of the more prominent characteristic lines; only a small fraction of *L* and *M* lines are shown.

ment the characteristic spectrum has a few lines at a relatively short wavelength, then an extended region in which there are no x-ray lines, followed in turn by a region in which there are a large number of lines, and so forth. The shortest wavelength and most penetrating lines emitted by an element are grouped in a narrow wavelength interval and are called the *K* lines; those in the next shorter wavelength region are called the *L* lines; for the heavier elements there are groups at still longer wavelengths called the *M* and *N* lines.

About 5 years before Moseley's work Barkla and his collaborators had clearly established the existence of characteristic radiation by absorption measurements. A schematic diagram of their experimental arrangements is shown in Fig. 7.9. A well-collimated beam of x-rays fell upon a block of material *E*, which absorbed the primary beam and

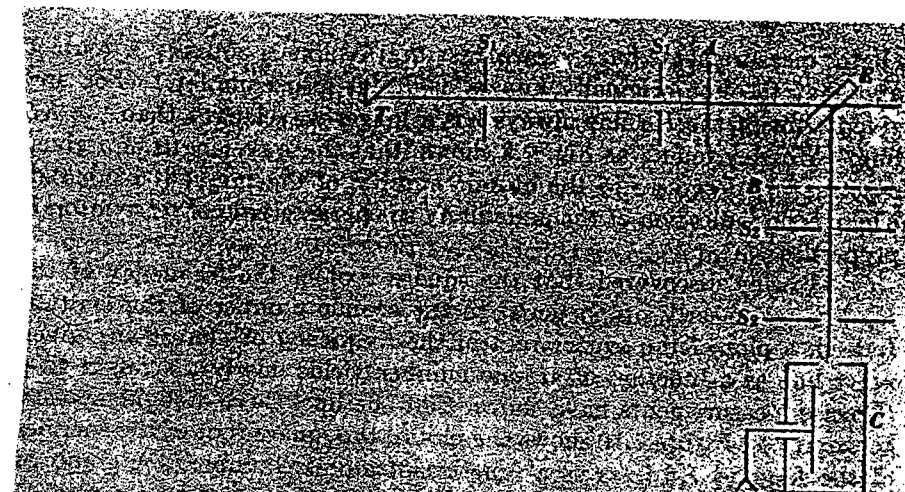


Fig. 7.9 Schematic arrangement for studying secondary radiation. Aluminum absorbing foils were inserted at *A* or at *B*.

emitted as secondary radiation its own characteristic x-rays. The fluorescent rays emitted at right angles to the primary beam were measured by an ionization chamber. The absorption coefficient of the radiation from the secondary emitter was determined by placing aluminum foils between *E* and the ionization chamber. A large number of materials were used as the secondary radiator; Barkla found that the greater the atomic weight, the more penetrating this secondary radiation. Even when the hardness of the primary beam was varied over a fairly broad range, the secondary radiation from a given material remained unchanged. However, when the voltage across the x-ray tube was reduced sufficiently, there came a point at which the characteristic radiation emitted by a radiator of high atomic number became much softer and more readily absorbed. With a further reduction in the hardness of the primary beam, the secondary radiation continued to have the same absorption coefficient. Thus, Barkla established the fact that secondary emitters of fairly high atomic number have characteristic radiation in at least two wavelength regions. He called the more penetrating rays the *K* radiation and the softer *L* radiation.

7.7 Moseley's Law

The *K* series of each element, as photographed by Moseley, appeared as two lines, the stronger of which was named *K α* and the weaker *K β* .

(Later measurements have shown that the $K\alpha$ line is actually a doublet and that the line originally known as $K\beta$ is also complex.) For any given element the $K\alpha$ line always has a longer wavelength than the $K\beta$ line. Moseley found, as Fig. 7.8 shows, that the wavelength of a given spectral line decreases as the atomic number of the target is increased. There is no indication of the periodicity so characteristic of many atomic properties.

Moseley discovered that the square root of the frequency of the $K\alpha$ line was nearly proportional to the atomic number of the emitter. Indeed, a plot of the square root of the frequency of almost any given x-ray line as a function of atomic number yields nearly a straight line. (Precise measurements have shown that the lines have a slight upward concavity.) Figure 7.10 shows the plot of the square root of the energies of the $K\alpha$ and $K\beta$ lines as a function of atomic number. A graph in which the square root of the frequency (usually multiplied by a constant) of an x-ray line is plotted as a function of atomic number is called a *Moseley plot*.

The frequency of the $K\alpha$ line for an element of atomic number Z can be represented very closely by the relation

$$\nu = 0.248 \times 10^{16} (Z - 1)^2 \text{ Hz} \quad (7.2)$$

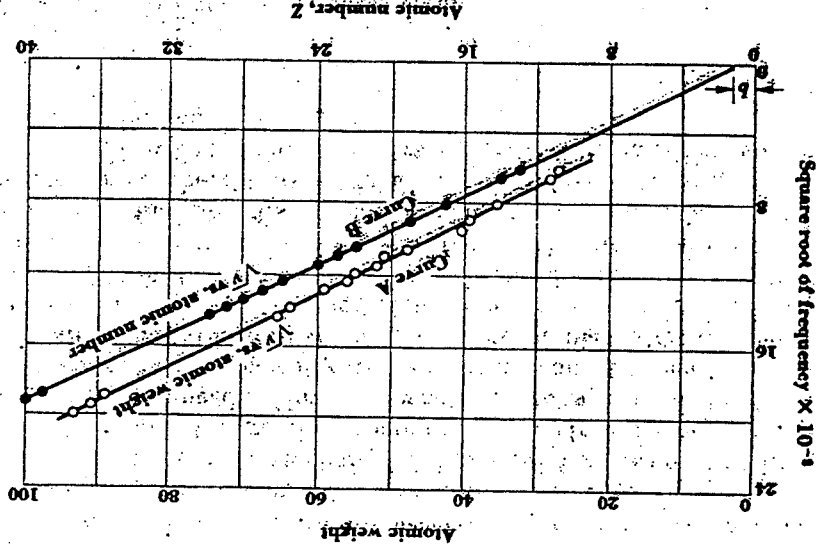


Fig. 7.10 Moseley's plot showing relation between the frequencies of x-ray lines and atomic number (Curve B), or atomic weight (Curve A).

For other lines it was found that an equation of the form

$$\nu = A(Z - \sigma)^2 \quad (7.2a)$$

gave reasonably good fits to experimental measurements. Here A and σ are constants for a given line. An explanation of Moseley's empirical relations was almost immediately available in terms of a theory developed by Bohr (Sec. 9.4).

One of the first important applications of Moseley's work was the resolution of several problems which were of great interest in connection with the periodic table. It was found that cobalt (at $w = 58.93$) is rather than nickel (at $w = 58.71$) is element number 27. Similarly it was confirmed that argon (at $w = 39.948$) should be placed before potassium (at $w = 39.102$), as had been suggested by chemists. Still another contribution was the observation that element 43 was missing and that ruthenium has atomic number 44. The observation of the $K\alpha$ series characteristic spectrum of any element is generally regarded as conclusive proof of the presence of this element in the target material. Ever since Moseley's work, any claim for the discovery of a new element has available a definitive check in the form of the proper $K\alpha$ x-ray spectrum, provided a large enough sample is available.

7.8 The Continuous X-ray Spectrum

Support for the hypothesis that electromagnetic radiation is emitted as photons of energy $h\nu$ came from the continuous x-ray spectrum. When high-energy electrons fall on a target, there is always a broad continuous spectrum of x-rays emitted as well as some characteristic lines. The general features of the continuous spectra from all sorts of target elements are essentially identical. Figure 7.11 shows the 1918 data of Ulrey for the continuous spectrum of wolfram (tungsten) for four potential differences applied to the x-ray tube. Here $I_0 d\lambda$ is the power emitted in the wavelength region between λ and $\lambda + d\lambda$.

Three features of the curves strike the eye immediately. 1. For each potential difference there exists a *short-wavelength limit*, i.e., the shortest wavelength emitted at a given tube potential difference is well defined, whereas on the long-wavelength side the intensity falls off gradually. In 1915 Duane and Hunt showed that the short-wavelength limit λ_{\min} is inversely proportional to the potential difference V . Clearly the maximum kinetic energy K_{\max} of an electron striking the target is V , and this is the largest energy that the electron can give up in producing electromagnetic radiation. If all this energy

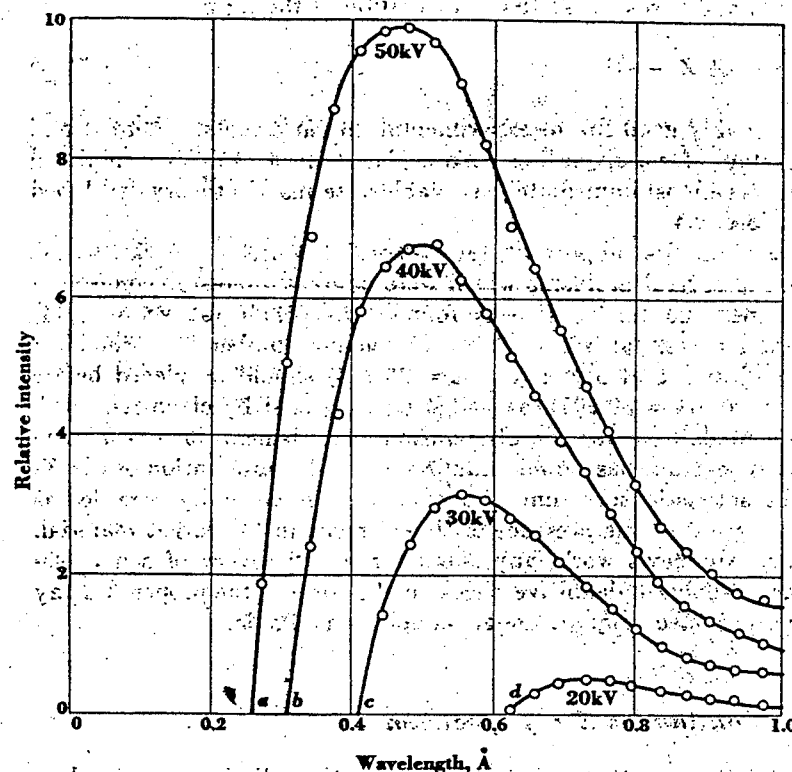


Fig. 7.11 Ulrey's curves for the distribution of energy in the continuous x-ray spectrum of tungsten.

goes to a single photon, the resulting frequency ν_{\max} and the corresponding wavelength λ_{\min} should, according to the Planck-Einstein theory, be given by

$$K_{\max} = Ve = h\nu_{\max} = \frac{hc}{\lambda_{\min}} \quad (7.3)$$

This relation, known as the *Duane-Hunt law*, led to one of the earliest reliable determinations of Planck's constant by Duane and his collaborators from data on λ_{\min} as a function of V .

Sometimes this phenomenon of the short-wavelength limit is called the *inverse photoelectric effect*. Here the kinetic energy of the incident electron is converted into radiant energy, while in the photoelectric effect radiant energy is converted, at least partially, into kinetic energy

of an electron. Whenever ϕ_0 is negligible compared with $h\nu$, Eqs. (6.11) and (7.3) take the same form.

Thus the quantum theory readily offers explanation of the short-wavelength limit of the continuous x-ray spectrum, a topic with which classical physics never dealt successfully.

2. The intensity of the continuous spectrum increases at all wavelengths as the potential difference across the tube is increased. The total x-ray power emitted is roughly proportional to the square of the potential difference V across the tube and to the atomic number Z of the target material. For ordinary x-ray potential differences the efficiency ϵ of x-ray production, defined as the ratio of x-ray power emitted to the power dissipated by the electron beam, is given approximately by

$$\epsilon \approx 1.4 \times 10^{-4} ZV$$

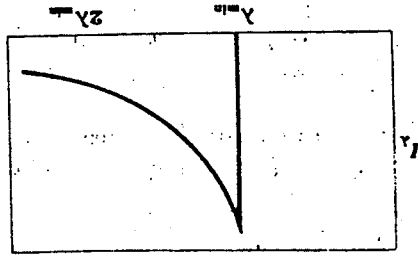
Most of the incident electrons in an x-ray tube do not lose all their kinetic energy in a single collision. A typical electron undergoes several collisions in a thick target, emitting quanta which have wavelengths longer than λ_{\min} .

3. As the potential difference V across the x-ray tube is increased, the wavelength at which the I_λ curve reaches its maximum moves toward shorter wavelengths. Ulrey found for the data of Fig. 7.11 that $\lambda_m \sqrt{V} = \text{const}$, where λ_m is the wavelength at which maximum energy is radiated. However, data obtained with other tubes are not always consistent with this equation. This is not surprising when one considers the complexity of the phenomenon. Some of the incident electrons penetrate into the target and radiate photons which may be absorbed before they escape, and so forth.

Thus far we have been discussing the continuous x-rays from a thick target. However, if the target is sufficiently thin—say of very thin gold foil—only a few of the electrons collide with atoms in it, most of them passing through the target undeviated. Thus slowly moving electrons will not be present in a *thin* target to the same degree as in a *thick* one. Accordingly, we expect that a greater proportion of the energy in the continuous spectrum from thin targets should lie near the λ_{\min} limit than from thick targets. This is in agreement with experiment.

In the continuous spectrum from a *very thin* target, experiment indicates, in agreement with the wave-mechanical computation of Sommerfeld, that the maximum of the energy-distribution curve occurs at the *limiting wavelength* λ_{\min} itself. On the short-wave side of λ_{\min} , the curve drops abruptly to the axis of abscissas, whereas toward longer waves it falls nearly in proportion to $1/\lambda^2$, as illustrated in Fig. 7.12. The curves for a thick target, as in Fig. 7.11, can be regarded as arising from

Fig. 7.12 Distribution of energy in the continuous x-ray spectrum from a very thin target.



the superposition of many elementary curves, such as that in Fig. 7.12, with various values of λ_{\min} . In such a target it might be expected that there would be a *most probable* type of collision which would correspond to the peak or maximum of the energy-distribution curve.

7.9 X-ray Scattering, Classical

The phenomenon of x-ray scattering has played an important part in theories of modern physics and has been the object of many researches, both theoretical and experiment. The first theory, proposed by J. J. Thomson, considered a plane-polarized electromagnetic wave moving along the z axis with its electric vector in the x direction (Fig. 7.13).

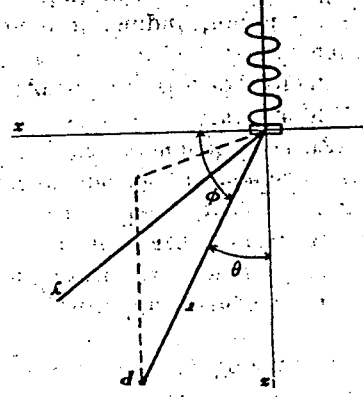


Fig. 7.13 An electron at the origin, set into harmonic oscillation by the electromagnetic wave from below, scatters a fraction of the incident intensity at angle θ .

$$E_s = \frac{ea \sin \phi}{4\pi\epsilon_0 r^2} \quad (7.4)$$

where r is the distance from the accelerated charge to P and ϕ is the angle between r and a . When $a = -eE/m$ is substituted, we have the magnitude of E_s

$$E_s = \frac{e^2 E \sin \phi}{4\pi\epsilon_0 m^2 r^2} \quad (7.5)$$

Since intensity is proportional to the square of the electric intensity, the ratio of the scattered intensity at P to the incident intensity is

$$\frac{I_s}{I_i} = \frac{E_s^2}{E_i^2} = \frac{16\pi^2\epsilon_0^2 m^2 c^4 r^2}{e^4 \sin^2 \phi} \quad (7.6)$$

If unpolarized radiation is incident on an electron, it is convenient to let r and the z axis fix the xz plane. The incident electric vector E can then be resolved into x and y components, which are equal on the average. For the x components $\sin \phi$ in Eq. (7.6) is equal to $\cos \theta$, while for the y components, $\sin \phi = 1$. The total intensity of the scattered wave at P is given by

$$I_s = \frac{16\pi^2\epsilon_0^2 m^2 c^4 r^2}{e^4} \left[\left(\frac{I}{2} \times 1 \right) + \left(\frac{I}{2} \times \cos^2 \theta \right) \right] = \frac{32\pi^2\epsilon_0^2 m^2 c^4 r^2}{e^4} (1 + \cos^2 \theta) \quad (7.7)$$

where θ is the angle between r and the z axis. Maxima in scattered intensity occur in the forward and backward directions; a minimum exists at $\theta = 90^\circ$. By integrating Eq. (7.7) over a sphere of radius r surrounding the electron, the scattered power P_s is found to be

$$P_s = \int_0^\pi I_s 2\pi r^2 \sin \theta d\theta = \frac{3}{8\pi} \left(\frac{4\pi\epsilon_0 m c^2}{e^2} \right)^2 I \quad (7.8)$$

where $e^2/4\pi\epsilon_0 m c^2$ is the classical radius of the electron [Eq. (2.16)].

The ratio of the power scattered to the primary intensity is called the *scattering cross section* (or *scattering coefficient*) of the free electron, designated by σ_e .

$$\sigma_e = \frac{8\pi}{3} \left(\frac{e^2}{4\pi\epsilon_0 mc^2} \right)^2 \quad (7.9)$$

The scattering coefficient has the dimensions of area; of the radiation incident on a unit area, the electron scatters the amount which would fall on the area σ_e , which has the numerical value $0.666 \times 10^{-28} \text{ m}^2$, or 0.666 barn ($1 \text{ barn} = 10^{-28} \text{ cm}^2 = 10^{-28} \text{ m}^2$). The Thomson (or classical) scattering coefficient is independent of wavelength. If each electron of an atom scatters independently, the atomic scattering cross section σ_a is the product of the atomic number of the atom and the electron cross section; $\sigma_a = Z\sigma_e$.

Thomson's theory predicts not only the intensity of the scattered beam but also its polarization. At $\theta = 0$ and $\theta = 180^\circ$, the scattered beam from an unpolarized incident beam is unpolarized, but at $\theta = 90^\circ$ the scattered beam is plane-polarized with electric vector in the y direction.

When a beam of x-rays of initial intensity I_0 passes through a thin layer of thickness Δx of any material, scattering by electrons in the layer changes the intensity by an amount

$$-\Delta I = \sigma I_0 \Delta x \quad (7.10)$$

where σ is called the *linear scattering coefficient* of the material. If each of the electrons of the material were to scatter independently of the others, the linear scattering coefficient would be

$$\sigma = n\sigma_e = \frac{8\pi}{3} \left(\frac{e^2}{4\pi\epsilon_0 mc^2} \right)^2 n \quad (7.11)$$

where n is the number of electrons per unit volume.

The ratio of σ to the density ρ of the scatterer is the *mass scattering coefficient* σ_m . For substances such as gases, the linear scattering coefficient depends, of course, on the density, but $\sigma_m = \sigma/\rho$ is constant. The first quantitative estimate of the number of electrons in an atom was made by Barkla and his coworkers in 1909 by applying Thomson's theory to data on the scattering of x-rays by carbon. They passed a beam of Mo $K\alpha$ x-rays through a graphite absorber and after correcting for photoelectric absorption found that the value of σ_m is approximately $0.02 \text{ m}^2/\text{kg}$ for carbon. If $\sigma = n\sigma_e$, then $\sigma_m = n\sigma_e/\rho$, and the number

of electrons per kilogram is

$$\begin{aligned} \frac{n}{\rho} &= \frac{\sigma_m}{\sigma_e} = \frac{0.02 \text{ m}^2/\text{kg}}{0.666 \times 10^{-28} \text{ m}^2/\text{electron}} \\ &= 3 \times 10^{26} \text{ electrons/kg} \end{aligned}$$

The number of carbon atoms per kilogram is the ratio of Avogadro's number N_A to the atomic weight A , or

$$\begin{aligned} \frac{N_A}{A} &= \frac{6.02 \times 10^{26} \text{ atoms/kmole}}{12 \text{ kg/kmole}} \\ &= 5 \times 10^{25} \text{ atoms/kg} \end{aligned}$$

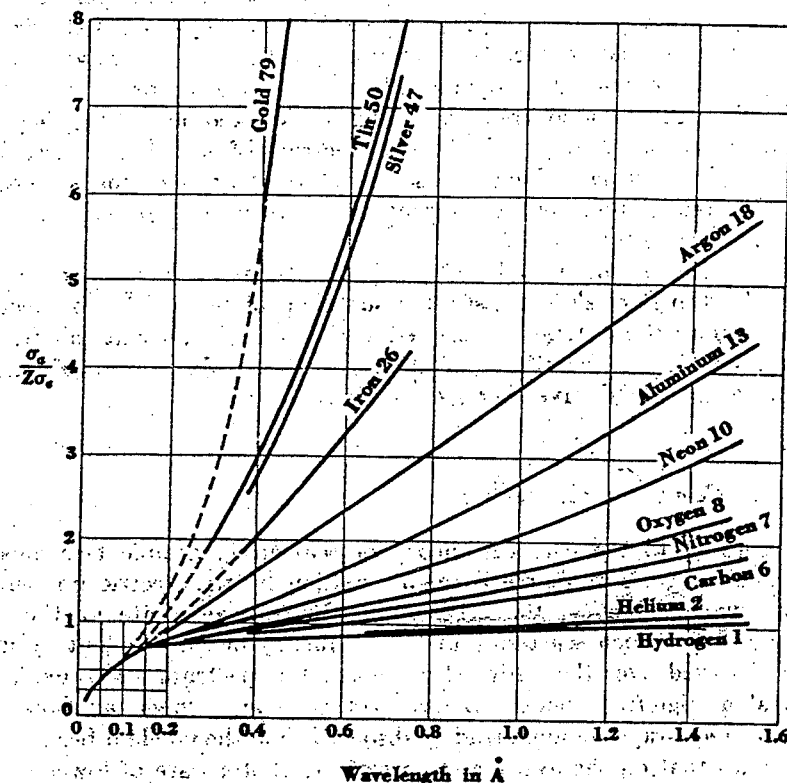


Fig. 7.14 Ratio of the scattering coefficients σ_a of various atoms to $Z\sigma_e$, the value which would pertain if each electron scattered independently with cross section σ_e . (Reproduced by permission of D. Van Nostrand Company, Inc., from Fig. III-3 in A. H. Compton and S. K. Allison, "X rays in Theory and Experiment," 1935.)

Hence the number of electrons per carbon atom must be 6. This determination was significant in the development of atomic theory, since it suggested the fact that the number of electrons per atom is less than the atomic weight and is perhaps about half of A .

Later measurements of scattering coefficients for $\lambda > 0.3 \text{ \AA}$ showed that for heavier elements the scattering coefficient σ exceeds nr , and hence the atomic scattering cross section σ_a is greater than $Z\sigma_r$ (Fig. 7.14). The excessive scattering is easily explained classically. When λ becomes comparable with the distances between electrons in an atom, they no longer scatter independently; the waves scattered by neighboring electrons are superposed more or less in the same phase, and so constructive interference occurs. As λ increases from a very small value, at first the inner (K) electrons scatter coherently; for longer wavelengths more electrons scatter nearly in phase. When λ is large compared to the atomic diameter, the relative phases of the waves from all Z electrons of an atom are small, and so the amplitude of the scattered wave from the atom is approximately proportional to Z and the scattered intensity to Z^2 . The theory of coherent scattering was worked out by Rayleigh, the cooperative scattering of the atomic electrons often being referred to as *Rayleigh scattering*. The decrease in σ at short wavelengths is predicted by the relativistic, quantum-mechanical treatment of scattering due to Klein and Nishina (Sec. 24.2).

From the curves of Fig. 7.14 one sees what fortuitous choices were involved in Barkla's successful measurement of the number of electrons per carbon atom. Had he selected a scatterer of higher atomic number or used $\text{Cu K}\alpha$ radiation (1.5 \AA) rather than $\text{Mo K}\alpha$ (0.707 \AA), his calculation would have been substantially in error.

7.10 Compton Scattering

According to the classical theory of scattering, atomic electrons are driven to perform simple harmonic motion by the electric intensity of the incident waves; the accelerated electrons reradiate at the same frequency. Such scattering at the frequency of the incident radiation is observed over the entire electromagnetic spectrum. However, it is weak at high frequencies. Before 1914, Gray and others had shown that scattered x-rays are more readily absorbed than the incident beam, which implies that on the average the scattered photons are of lower energy. In 1923 Compton published the results of careful measurements of the x-ray frequencies scattered by carbon atoms upon which monochromatic x-rays were incident. He found that the scattered beam contained *two frequencies*, one the same as that of the incident beam and the

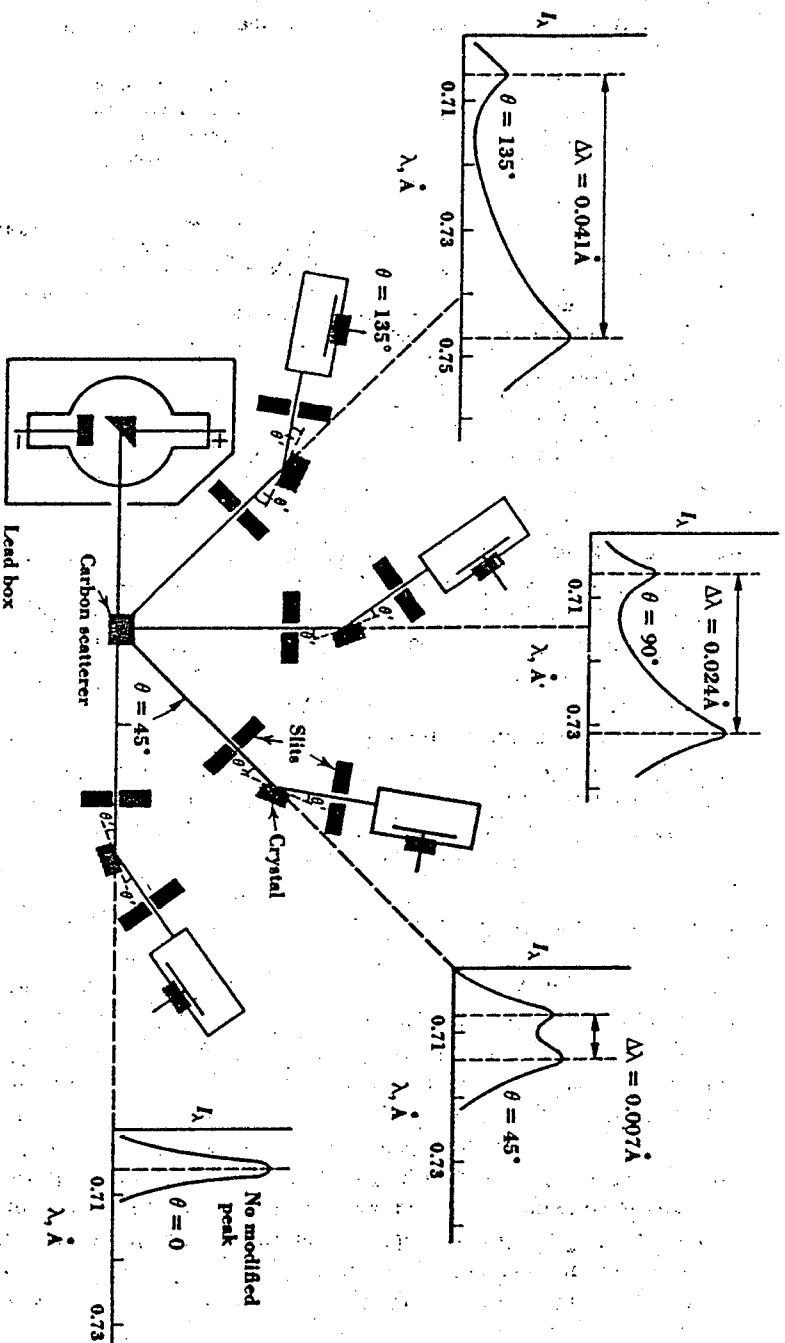


Fig. 7.15 The scattering of $\text{Mo K}\alpha$ x-rays ($\lambda = 0.707 \text{ \AA}$) at an angle θ gives rise to two peaks in the scattered radiation, one at the incident wavelength and the second at a wavelength greater by $\Delta\lambda = 0.024(1 - \cos \theta) \text{ \AA}$. (After A. W. Smith and J. N. Cooper, "Elements of Physics," 7th ed. Copyright 1964. McGraw-Hill Book Company. Used by permission.)

second somewhat lower. On the basis of the quantum theory of radiation, Compton derived a relation which quantitatively predicted scattering at the observed lower frequency. This *Compton effect* represents one of the most conclusive evidences of the particle properties of electromagnetic radiation and probably convinced more physicists that quantum mechanics should be accepted than any other experiment.

Compton used a graphite block to scatter Mo $K\alpha$ radiation and measured the wavelength of the scattered photons with a Bragg spectrometer (Fig. 7.15). At each finite scattering angle, he observed two peaks in the scattered beam, one at the incident wavelength 0.707 \AA and the second at a wavelength longer by an amount $\Delta\lambda$ dependent on the scattering angle θ , according to the relation $\Delta\lambda = 0.024(1 - \cos \theta) \text{ \AA}$. Compton subsequently showed that $\Delta\lambda$ is independent of the scattering material.

To explain the occurrence of the shifted component, Compton boldly applied the quantum picture of radiant energy. He assumed that the scattering process could be treated as an elastic collision between a photon and an electron, governed by the two laws of mechanics, the conservation of energy and the conservation of momentum. Let an incident photon of energy $h\nu$ collide with an electron initially at rest. The photon is scattered through an angle θ , while the electron recoils in a direction ϕ (Fig. 7.16). The kinetic energy K given to the electron is $(m - m_0)c^2$ by Eq. (2.12). If ν_s is the frequency of the scattered photon, the conservation of energy requires that the sum of the kinetic energy of the electron and the energy of the scattered photon be equal

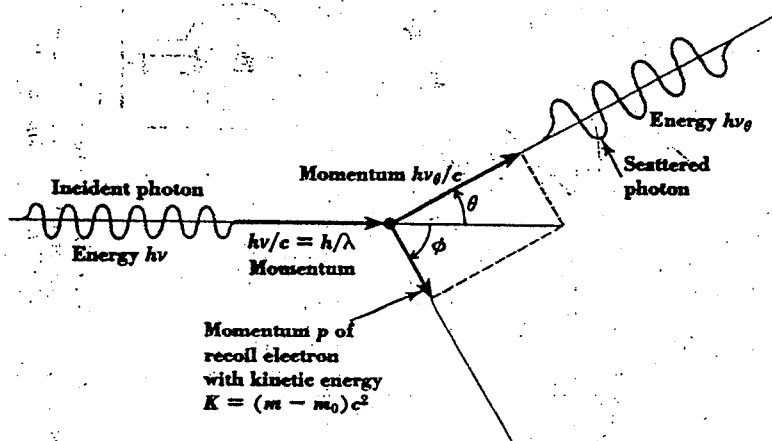


Fig. 7.16 Elastic collision of a photon with electron initially at rest.

to the energy of the incident photon, or

$$h\nu = h\nu_s + (m - m_0)c^2 \quad (7.12)$$

Each photon carries momentum equal to its energy $h\nu$ divided by the speed of light c , or h/λ . Since momentum is a vector quantity and is conserved, the x and y components (Fig. 7.16) must obey the equations

$$\frac{h\nu}{c} = \frac{h\nu_s}{c} \cos \theta + p \cos \phi \quad (7.13a)$$

$$0 = \frac{h\nu_s}{c} \sin \theta + p \sin \phi \quad (7.13b)$$

where p is the momentum of the recoil electron. (The plus sign appears with $\sin \phi$ because it is assumed all angles are positive when measured counterclockwise from the x axis; thus in Fig. 7.16 ϕ is a negative angle.)

If we introduce the wavelength of the two photons through $\nu/c = 1/\lambda$ and recall that $p = m_0 v / \sqrt{1 - (v/c)^2}$, we may rewrite Eqs. (7.13a, b) thus:

$$\frac{h}{\lambda} - \frac{h \cos \theta}{\lambda_s} = \frac{m_0 v \cos \phi}{\sqrt{1 - (v/c)^2}} \quad \frac{h}{\lambda_s} \sin \theta = - \frac{m_0 v \sin \phi}{\sqrt{1 - v^2/c^2}}$$

Squaring these two equations and adding them eliminates ϕ and leaves

$$\frac{h^2}{\lambda^2} + \frac{h^2}{\lambda_s^2} - \frac{2h^2}{\lambda\lambda_s} \cos \theta = \frac{m_0^2 v^2}{1 - (v/c)^2} = \frac{m_0^2 c^2}{1 - (v/c)^2} - m_0^2 c^2 \quad (7.14)$$

Similarly, Eq. (7.12) can be divided by c and written

$$\frac{h}{\lambda} - \frac{h}{\lambda_s} + m_0 c = \frac{m_0 c}{\sqrt{1 - (v/c)^2}} \quad (7.12a)$$

and squared to give

$$\frac{h^2}{\lambda^2} + \frac{h^2}{\lambda_s^2} - \frac{2h^2}{\lambda\lambda_s} + 2m_0 c h \left(\frac{1}{\lambda} - \frac{1}{\lambda_s} \right) + m_0^2 c^2 = \frac{m_0^2 c^2}{1 - v^2/c^2} \quad (7.15)$$

Subtracting Eq. (7.14) from (7.15) yields

$$\frac{2h^2}{\lambda\lambda_s} (1 - \cos \theta) - 2m_0 c h \left(\frac{1}{\lambda} - \frac{1}{\lambda_s} \right) = 0$$

or

$$\Delta\lambda = \lambda_e - \lambda = \frac{h}{m_0c} (1 - \cos \theta) \quad \text{A}$$

(7.16)

Thus, the wavelength shift predicted by Compton's theory is in excellent agreement with the experimental results. Compton scattering reveals the particle characteristics of photons.

The quantity h/m_0c is known as the *Compton wavelength* of the electron; it corresponds to the wavelength of a photon with energy equal to the rest energy m_0c^2 of the electron. It is sometimes useful to extend this idea to other particles; thus the Compton wavelength of a proton of rest mass M_p is $h/M_p c$.

The Compton shift in wavelength, Eq. (7.16), depends on the scattering angle but is independent of the energy of the incident photon. On the other hand, the energy difference between incident and scattered photon increases rapidly as the energy of the incident photon is raised, as can be readily found by rewriting Eq. (7.16) in the form

$$\frac{1}{\lambda} - \frac{1}{\lambda'} = \frac{m_0c}{h} (1 - \cos \theta) \quad (7.16a)$$

In Compton's experimental work there appeared not only a modified line but also a line with the same wavelength as the primary. This unmodified line can be explained in terms of the photon concept as the result of a collision of a photon with a bound electron, held sufficiently tightly for an entire atom (or even an entire crystal) to recoil. In such a collision the predicted wavelength shift is given by replacing m_0 by the mass of the recoiling atom in Eq. (7.16) and is so small as to be unobservable for typical x-ray photons. The substantially greater breadth of the modified line compared to the unmodified line can be explained satisfactorily in terms of the fact that most scattering electrons are not initially at rest but have a range of initial momenta and energies.

7.11 Compton Recoil Electrons

The recoil electrons predicted by Compton's theory were promptly looked for and found by C. T. R. Wilson and by Bothe. The kinetic energy $K = (m - m_0)c^2$ of the recoil electrons is given by Eq. (7.12)

(7.12b)

The Compton or modified line is very broad at comparatively low frequencies. This breadth can be thought of as caused by the motion of the electrons in the atom. In our simple deduction of the Compton effect, the electron was assumed to be initially at rest; if it is assumed to have a component of velocity, positive or negative, in

Through out this discussion the conventional assumption has been made that the recoil electron was initially unbound and at rest, an approximation which is tenable only when the kinetic energy acquired by the recoil electron is much greater than the energy with which it is bound to its atom. The effect of the binding is to reduce $\Delta\lambda$ slightly. In addition to the Compton process, in which the electron is freed from the atom, there are also *Snekal-Raman* processes, in which the frequency of the scattered radiation is changed by an amount which corresponds to transition between two bound states of the scattering atom.

Compton's theory is based on the assumption that the recoil of the electron occurs simultaneously with the scattering of the photon and that both energy and momentum are conserved in the collision. The *simultaneity* and *conservation* requirements have been tested experimentally with great care by several observers by use of scintillation detectors and coincidence techniques. One detector fixes θ and measures $h\nu$ for the photon, while a second detector gives ϕ and K for the recoil electron. Within experimental error, for every Compton photon scattered at an angle θ there is a recoil electron at angle ϕ given by Eq. (7.18) with kinetic energy given by Eq. (7.17b). The simultaneity time limit is less than 2×10^{-11} s in many experiments and in some cases less than 10^{-11} s.

$$\cot \phi = (1 + \epsilon) \tan \frac{\theta}{2} \quad (7.18)$$

By 1927 Bless, using the magnetic spectrograph, showed that the observed values of K for the recoil electrons are in agreement with the theory. The relation between the scattering angles, ϕ for the electron and θ for the photon, is given by

$$K = h\nu \frac{\epsilon(1 - \cos \theta)}{1 + \epsilon(1 - \cos \theta)} \quad (7.17a)$$

$$K = h\nu \frac{(1 + \epsilon)^2 - \epsilon^2 \cos^2 \phi}{2\epsilon \cos^2 \phi} \quad (7.17)$$

If ϵ represents $h\nu/m_0c^2$, it can be shown that

the direction of the incident radiation, the wavelength shift is different. Wave mechanics furnishes a probability distribution for the velocities of the atomic electrons, from which the broadening can be computed, in agreement with experiment. As ν is then increased further, the Compton line becomes narrower. Eventually, in any direction of scattering other than that of the incident beam, the unmodified line becomes weaker than the Compton line, sooner at large angles of scattering than at small angles, and sooner for heavy atoms than for light ones. Finally, only the modified line remains in appreciable intensity.

7.12 The Nature of Electromagnetic Radiation

The question as to the true nature of electromagnetic radiation arises in its sharpest form in contemplating the contrasting properties of x-rays. How can an entity exhibit the wave behavior that is evidenced in the diffraction of x-rays by crystals and, on the other hand, the particle properties that are revealed by the Compton effect?

According to quantum mechanics, as interpreted by Bohr and other theoretical physicists, the riddle can be solved only by extending to radiation a limitation upon the use of ordinary space-time conceptions. Bohr insisted that whenever an observation of any sort is made, its *immediate* result is always expressible in terms of familiar ideas of space and time, since these ideas have been developed out of human experience and any observation necessarily includes as its primary stage a certain experience by a human observer. But it does not follow that it will always be possible to construct a picture of the physical reality that causes these experiences in the same way in which we picture everyday objects. In classical theory, an electromagnetic field was assumed to have a certain character at every point in space and at every instant of time, as represented by certain values of the electric and magnetic vectors. According to the new view, such a conception of the electromagnetic field is valid at best as an approximation.

The essential significance of what we call a radiation field lies in its effects upon the motion of charged particles. It is possible for the field to exhibit contrasting characteristics under different circumstances. At one extreme, the action of the field takes the form with which we have become familiar in the Compton effect. Here a photon appears to bounce off an electron, thereby changing the momentum of the electron suddenly and discontinuously. The change of momentum Δp will be definitely observable and measurable by the physicist

only if it considerably exceeds the range of indeterminateness of the momentum already possessed by the particle. A clear-cut scattering process of the Compton type can occur only when the wavelength of the radiation is shorter than the diameter of the region in which the particle may be supposed to be effectively localized. For an electron in an atom, this condition can be met only for wavelengths considerably shorter than the atomic diameter, such as the wavelengths of hard x-rays or γ rays.

In the Compton process there is no feature that can be regarded as a manifestation of an electric intensity in the wave. In order to obtain, at the opposite extreme, an action of radiation that can be interpreted in terms of the familiar electric and magnetic vectors, two conditions must be met. The experimental conditions must be such that it is possible to follow the test particle in effectively continuous motion along a path so that its acceleration can be determined. It is also necessary that a segment of path which is sufficiently long to permit an adequate determination of the acceleration shall yet be short enough to ensure that along it the field vectors do not vary appreciably in value. Thus the familiar action ascribable to electric and magnetic fields in the radiation is obtained only when the particle acted on is definitely located within a region much smaller than a wavelength. This latter condition is satisfied, for example, by the electrons in a wire held parallel to the electric vector in long electromagnetic waves. In such a wire alternating electric current is observed to be produced, varying in phase with the electric vector. Ions in the upper atmosphere acted on by such waves furnish another example.

In such cases the magnetic field in the waves will also act upon the current or on the moving ions. It thus comes about that the average result is a force in the direction of propagation of the waves. This force constitutes an example of light pressure, and it can be regarded as analogous to the Compton recoil that occurs under other circumstances; but here there is a continuous rather than a discontinuous action.

Problems

1. Find the grating space for KBr and KCl, which have densities of 2750 and 1984 kg/m³ respectively.

Ans: 3.30 Å; 3.14 Å

2. Find the wavelength for which first-order Bragg reflection occurs at a 20° glancing angle from calcite. At which angle does second-order

reflection occur? What is the glancing angle for Mo $K\alpha$ radiation (0.707 Å) in first order?

Ans: 2.076 Å; 43.2°; 6.7°

3. An x-ray tube with a copper target is operated at a potential difference of 25 kV. The glancing angle with a NaCl crystal for the $\text{Cu } K\alpha$ line is found to be 15.8°. Find the wavelength of this line and the glancing angle for photons at the short-wavelength limit.

Ans: 1.54 Å; 5.1°

4. An x-ray tube with a tungsten target is operated with a dc power supply giving 15 mA at a potential difference of 60 kV. What is the short-wavelength limit of the x-rays produced? Estimate the approximate power radiated in x-rays.

Ans: 0.207 Å; about 6 W

5. Find the short-wavelength limit for x-radiation from (a) a television tube operated at 10 kV, (b) an x-ray tube operated at 100 kV, (c) a 20-MeV betatron, and (d) a 1-GeV linear electron accelerator.

Ans: 1.24 Å; 0.124 Å; 0.62 XUV; 0.0124 XUV

6. Find the short-wavelength limit for the radiation from (a) an x-ray tube operated at 30 kV, (b) a 50-MeV electron linac (linear accelerator), and (c) a 300-MeV synchrotron.

7. One of the best proofs for the discovery of a new element lies in obtaining the characteristic x-ray spectrum predicted for that element. Plot a Moseley graph for the $K\alpha$ line and predict to three significant figures the wavelength of this line for elements 85, 87, and 94.

Ans: 0.150, 0.147, 0.135 Å

8. Assuming that all scattering is of the incoherent Thomson variety, find the atomic, mass, and linear scattering coefficients for copper. Judging by Fig. 7.14, at what wavelength would you expect these values to be approximately correct? At $\lambda = 0.707$ Å (Mo $K\alpha$) what would you estimate σ_a to be for Cu?

9. Unpolarized x-rays undergo Thomson scattering at a graphite block. Find the polarization of the radiation scattered in the xz plane at $\theta = 30^\circ$. (The polarization is defined as

$$P = \frac{I_{\perp} - I_{\parallel}}{I_{\perp} + I_{\parallel}}$$

where I_{\perp} and I_{\parallel} refer to the intensities scattered with the electric vector respectively normal and parallel to the xz plane.)

10. X-rays of $\lambda = 0.085$ Å are scattered by carbon. At what angle will Compton scattered photons have a wavelength of 0.090 Å?

Ans: 37.5°

11. A photon is Compton scattered by an electron through an angle of 90°. Find the energy of the scattered photon for incident-photon energies of 10 keV, 0.511 MeV, and 10 MeV.

Ans: 0.0098, 0.256, and 0.486 MeV

12. Show that the kinetic energy of a Compton scattered electron is given by Eq. (7.17) in terms of ϕ or by Eq. (7.17a) in terms of θ .

13. Find the smallest energy a photon may have and still transfer one-half of its energy to an electron initially at rest.

Ans: 256 keV

14. Show that the recoil angle for a Compton electron is given by

$$\cos \phi = \frac{(h\nu)^2 - (h\nu')^2 + p^2 c^2}{2h\nu p c}$$

where p is the momentum of the electron.

15. A cosmic-ray photon of energy $h\nu$ is scattered through 90° by an electron initially at rest. The scattered photon has a wavelength twice that of the incident photon. Find the frequency of the incident photon and the recoil angle of the electron.

Ans: 1.2×10^{10} Hz; 26.6°

16. Derive Eq. (7.18).

17. A photon of high energy $h\nu$ makes a head-on collision with a free electron at rest.

(a) Apply the conservation laws to this collision to show that $2h\nu = K + \sqrt{K^2 + 2m_0 c^2 K}$, where K is the kinetic energy of the recoil electron.

(b) If $h\nu = 10$ MeV, find K .

Ans: 9.75 MeV

18. For a photon which has undergone Compton scattering, show that the energy is

$$h\nu' = \frac{h\nu}{1 + \epsilon(1 - \cos \theta)}$$

where $\epsilon = h\nu/m_0 c^2$.

19. A 0.511-MeV photon strikes an electron head on and is scattered straight backward. Find the energy of the scattered photon, the energy of the recoil electron, and the ratio v/c for the latter.

20. If in a Compton scattering the recoil electron moves off at angle ϕ , show that the photon recoils at an angle θ given by

$$\cos \theta = 1 - \frac{(1 + \epsilon)^2 \tan^2 \phi + 1}{2}$$

21. Verify that a freely moving electron cannot spontaneously emit or absorb a photon.
22. When a high-energy photon undergoes Compton scattering at an angle of 30° , the recoil electron is projected with $\phi = 30^\circ$. Find the energy of the incident photon.

Ans: 2.78 MeV

23. (a) The average intensity of a beam of plane-polarized electromagnetic radiation is $\frac{1}{2}c\epsilon_0 E_0^2$, where E_0 is the amplitude of the electric vector. Calculate the classical amplitude of vibration of a free electron under the influence of a beam of x-rays with wavelength 0.7 \AA and an intensity of 20 W/m^2 .

(b) What power is reradiated as scattered x-radiation by the electron?

(c) Find the intensity required to give the electron an amplitude of 0.05 \AA .

24. A spectrometer to determine the energy of incident γ rays operates as follows. Collimated γ rays strike a thin target, and Compton recoil electrons proceeding in the direction of the original γ 's are analyzed magnetically. (Note that the Compton scattering angle is then 180° .) If r is the radius of the electron's path and B is the magnetic induction, derive a relativistically correct equation for the γ -ray energy in terms of r , B , and fundamental constants.

25. In the inverse Compton effect a photon gains energy in an elastic collision with a high-energy electron. If in the laboratory reference frame, a 10-eV photon collided head on with a 500-MeV electron, find the energy of the Compton scattered photon in the laboratory system.

26. One means of producing monoergic photons with high energy (and nearly 100 percent polarization) is through the inverse Compton effect (see Prob. 25). If an intense laser beam of 6942-\AA photons is made to collide head on with a beam of 20-GeV electrons, find (a) the energy of the incident photons in a reference frame moving with the electrons, and (b) the energy of the back-scattered photons in the laboratory reference frame. Some of the high-energy photons observed in cosmic rays may have gained energy through the inverse Compton process.

chapter eight

Radioactivity and the Nuclear Atom

The discovery of radioactivity by Henri Becquerel in 1896 marks the starting point of nuclear physics. As a result of his work and the investigations by the Curies, Rutherford and his collaborators, and many others, it became evident that this phenomenon involves the operation of forces of a different order of magnitude from any familiar to chemists or physicists of that time and that one was dealing with the actual transmutation of the elements, for which men had searched in vain since the time of the Egyptians. As a direct outgrowth of these studies came the identification of a host of materials possessing the remarkable property of spontaneously transforming from one into another, and with the unraveling of these successive transformations came the first clue to the intimate relation between the elements. Exploitation of the enormously energetic radiations which these substances emitted led to the discovery of the nucleus itself, to the nuclear model of the atom, and finally to the artificially induced transmutation of the stable elements.

respect to Δx or Δp_x in part (b). Note that classically the minimum energy would be zero.)

33. A TV tube manufacturer is attempting to improve the picture resolution, while keeping costs down, by designing an electron gun that produces an electron beam which will make the smallest possible spot on the face of the tube, using only an electron emitting cathode followed by a system of two well-spaced apertures. (a) Show that there is an optimum diameter for the second aperture. (b) Using reasonable TV-tube parameters, estimate the minimum possible spot size.
34. A boy on top of a ladder of height H is dropping marbles of mass m to the floor and trying to hit a crack in the floor. To aim, he is using equipment of the highest possible precision. (a) Show that the marbles will miss the crack by an average distance of the order of $(h/m)^{1/2}(H/g)^{1/4}$, where g is the acceleration due to gravity. (b) Using reasonable values of H and m , evaluate this distance.
35. Show that in order to be able to determine through which slit of a double-slit system each photon passes without destroying the double-slit diffraction pattern, the condition $\Delta y \Delta p_y \ll h/2$ must be satisfied. Since this condition violates the uncertainty principle, it cannot be met.

EISBERG - RESNICK

QUANTUM PHYSICS

4

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4-1 THOMSON'S MODEL

By 1910 experimental evidence had been accumulated which showed that atoms contain electrons (e.g., scattering of x rays by atoms, photoelectric effect, etc.). These experiments also provided an estimate of Z , the number of electrons in an atom. They found it to be roughly equal to $A/2$, where A is the chemical atomic weight of the atom in question. Since atoms are normally neutral, they must also contain positive charge equal in magnitude to the negative charge carried by their normal complement of electrons. Thus a neutral atom has a negative charge $-Ze$, where $-e$ is the electron charge, and also a positive charge of the same magnitude. That the mass of an electron is very small compared to the mass of even the lightest atom implies that most of the mass of the atom must be associated with the positive charge.

These considerations naturally led to the question of the distribution of the positive and negative charges within the atom. J. J. Thomson proposed a tentative description, or *model*, of an atom according to which the negatively charged electrons were located within a continuous distribution of positive charge. The positive charge distribution was assumed to be spherical in shape with a radius of the known order of magnitude of the radius of an atom, 10^{-10} m. (This value can be obtained from the density of a typical solid, its atomic weight, and Avogadro's number.) Owing to their mutual repulsion, the electrons would be uniformly distributed through the sphere of positive charge. Figure 4-1 illustrates this "plum pudding" model of the atom. In an atom in its lowest possible energy state, the electrons would be fixed at their equilibrium positions. In excited atoms (e.g., atoms in a material at high temperature), the electrons would vibrate about their equilibrium positions. Since classical electromagnetic theory predicts that an accelerated charged body, such as a vibrating electron, emits electromagnetic radiation, it was possible to understand qualitatively the emission of such radiation by excited atoms on the basis of Thomson's model. Quantitative agreement with experimentally observed spectra was lacking, however.

Example 4-1. (a) Assume that there is one electron of charge $-e$ inside a spherical region of uniform positive charge density ρ (a Thomson hydrogen atom). Show that its motion, if it has kinetic energy, can be simple harmonic oscillation about the center of the sphere.

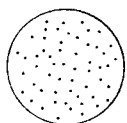


Figure 4-1 Thomson's model of the atom—a sphere of positive charge embedded with electrons.

► Let the electron be displaced to a distance a from the center, with a less than the radius of the sphere. From Gauss's law, we know that we can calculate the force on it by using Coulomb's law

$$F = -\frac{1}{4\pi\epsilon_0} \left(\frac{4}{3}\pi a^3 \rho \right) \frac{e}{a^2} = -\frac{\rho e a}{3\epsilon_0}$$

where $(4/3)\pi a^3 \rho$ is the net positive charge in a sphere of radius a . Hence, we can write $F = -ka$, where the constant $k = \rho e/3\epsilon_0$. If the electron at a is freed with no initial velocity, this force will produce simple harmonic motion along a diameter of the sphere since it is always directed towards the center and has a strength which is proportional to the displacement from the center. ◀

(b) Let the total positive charge have the magnitude of one electron charge (so that the atom has no net charge), and let it be distributed over a sphere of radius $r' = 1.0 \times 10^{-10}$ m. Find the force constant k and the frequency of the motion of the electron.

► We have

$$\rho = \frac{e}{\frac{4}{3}\pi r'^3}$$

so that

$$k = \frac{\rho e}{3\epsilon_0} = \frac{e}{\frac{4}{3}\pi r'^3} \frac{e}{3\epsilon_0} = \frac{e^2}{4\pi\epsilon_0 r'^3} \\ = \frac{9.0 \times 10^9 \text{ nt}\cdot\text{m}^2/\text{coul}^2 \times (1.6 \times 10^{-19} \text{ coul})^2}{(1.0 \times 10^{-10} \text{ m})^3} = 2.3 \times 10^2 \text{ nt/m}$$

The frequency of the simple harmonic motion is then

$$v = \frac{1}{2\pi} \sqrt{\frac{k}{m}} = \frac{1}{2\pi} \sqrt{\frac{2.3 \times 10^2 \text{ nt/m}}{9.11 \times 10^{-31} \text{ kg}}} = 2.5 \times 10^{15} \text{ sec}^{-1}$$

Since (in analogy to radiation emitted by electrons oscillating in an antenna) the radiation emitted by the atom will have this same frequency, it will correspond to a wavelength

$$\lambda = \frac{c}{v} = \frac{3.0 \times 10^8 \text{ m/sec}}{2.5 \times 10^{15} \text{ /sec}} = 1.2 \times 10^{-7} \text{ m} = 1200 \text{ Å}$$

in the far ultraviolet portion of the electromagnetic spectrum. It is easy to show that an electron moving in a stable circular orbit of any radius inside the Thomson atom revolves at this same frequency, and so it would radiate at this frequency also.

Of course, a different assumed radius of the sphere of positive charge would give a different frequency. But the fact that a Thomson hydrogen atom has only one characteristic emission frequency conflicts with the very large number of different frequencies observed in the spectrum of hydrogen. ◀

Conclusive proof of the inadequacy of Thomson's model was obtained in 1911 by Ernest Rutherford, a former student of Thomson's, from the analysis of experiments on the scattering of α particles by atoms. Rutherford's analysis showed that, instead of being spread throughout the atom, the positive charge is concentrated in a very small region, or *nucleus*, at the center of the atom. This was one of the most important developments in atomic physics and was the foundation of the subject of nuclear physics.

Rutherford had already been awarded the Nobel Prize in 1908 for his "investigations in regard to the decay of elements and . . . the chemistry of radioactive substances." He was a talented, hard-working physicist with enormous drive and self-confidence. In a letter written later in life, the then Lord Rutherford wrote, "I've just been reading some of my early papers and, you know, when I'd finished, I said to myself, 'Rutherford, my boy, you used to be a damned clever fellow.'" Though pleased at winning a Nobel Prize he was not happy that it was a chemistry prize, rather than one in physics. (Any research in the elements was then

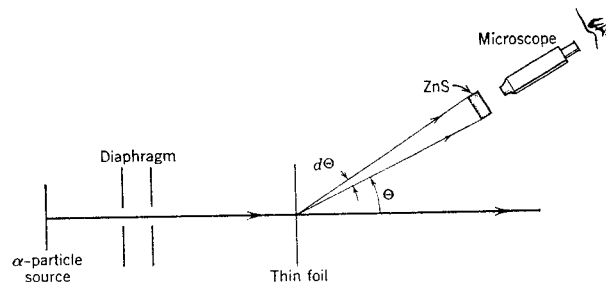


Figure 4-2 Arrangement of an α -particle scattering experiment. The region traversed by the α particles is evacuated.

considered chemistry.) In his speech accepting the prize he noted that he had observed many transformations in his work with radioactivity but never had seen one as rapid as his own, from physicist to chemist.

Rutherford already knew α particles to be doubly ionized helium atoms (i.e., He atoms with two electrons removed), emitted spontaneously from several radioactive materials at high speed. In Figure 4-2 we show a typical arrangement that he and his colleagues used to study the scattering of α particles on passing through thin foils of various substances. The radioactive source emits α particles which are collimated into a narrow parallel beam by a pair of diaphragms. The parallel beam is incident upon a foil of some substance, usually a metal. The foil is so thin that the particles pass completely through with only a small decrease in speed. In traversing the foil, however, each α particle experiences many small deflections due to the Coulomb force acting between its charge and the positive and negative charges of the atoms of the foil. Since the deflection of an α particle in passing through a single atom depends on the details of its trajectory through the atom, the net deflection in passing through the entire foil will be different for different α particles in the beam. As a result, the beam emerges from the foil not as a parallel beam but as a divergent beam. A quantitative measure of its divergence is found by measuring the number of α particles scattered into each angular range Θ to $\Theta + d\Theta$. The α particle detector consisted of a layer of the crystalline compound ZnS and a microscope. The crystal ZnS has the useful property of producing a small flash of light when struck by an α particle. If observed with a microscope, the flash due to the incidence of a *single* α particle can be distinguished. In the experiment an observer counts the number of light flashes produced per unit time as a function of the angular position of the detector.

Let N represent the number of atoms that deflect an α particle in its passage through the foil. If θ represents the angle of deflection in passing through one atom, as in Figure 4-3, and Θ is the net deflection in passing through all the atoms in its

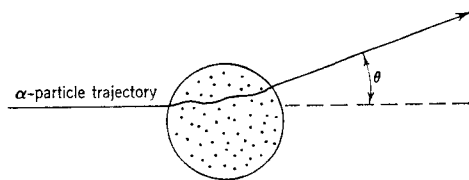


Figure 4-3 An α particle passing through a Thomson model atom. The angle θ specifies the deflection of the α particle.

trajectory through the foil, then statistical theory shows that

$$(\bar{\Theta}^2)^{1/2} = \sqrt{N} (\bar{\theta}^2)^{1/2} \quad (4-1)$$

Here $(\bar{\Theta}^2)^{1/2}$ is the root mean square net deflection, or scattering, angle and $(\bar{\theta}^2)^{1/2}$ is the root mean square scattering angle in a deflection from a single atom. The factor \sqrt{N} comes from the randomness of the deflection; if all deflections were in the same direction, clearly we would obtain N instead of \sqrt{N} . More generally, statistical theory gives the following angular distribution of the scattered α particles

$$N(\Theta)d\Theta = \frac{2I\Theta}{\bar{\Theta}^2} e^{-\Theta^2/\bar{\Theta}^2} d\Theta \quad (4-2)$$

where $N(\Theta)d\Theta$ is the number of α 's scattered within the angular range Θ to $\Theta + d\Theta$, and I is the number of α 's passing through the foil.

Because electrons have a very small mass compared to the α particle, they can in any case produce only small α -particle deflections; and because the positive charge is distributed over all the volume of the $r' \approx 10^{-10}$ m radius Thomson atom it cannot provide a Coulomb repulsion intense enough to produce a large deflection of the α particle. Indeed, using Thomson's model we find that the deflection caused by one atom is $\theta \approx 10^{-4}$ rad. This result and (4-1) and (4-2) comprise the α -particle scattering predictions of the Thomson model of the atom. Rutherford and his group tested these predictions.

Example 4-2. (a) In a typical experiment (Geiger and Marsden, 1909), α particles were scattered by a gold foil 10^{-6} m thick. The average scattering angle was found to be $(\bar{\Theta}^2)^{1/2} \approx 1^\circ \approx 2 \times 10^{-2}$ rad. Calculate $(\bar{\theta}^2)^{1/2}$.

► The number of atoms traversed by the α particle is approximately equal to the thickness of the foil divided by the diameter of the atom. Hence

$$N \approx 10^{-6} \text{ m} / 10^{-10} \text{ m} = 10^4$$

The average deflection angle in traversing a single atom then, from (4-1), is

$$(\bar{\theta}^2)^{1/2} = \frac{(\bar{\Theta}^2)^{1/2}}{\sqrt{N}} \approx \frac{2 \times 10^{-2}}{10^2} \approx 2 \times 10^{-4} \text{ rad}$$

not in disagreement with the Thomson atom estimate $\theta \approx 10^{-4}$ rad. ◀

(b) More than 99% of the α particles were scattered at angles less than 3° . The measurements, using 1° for $(\bar{\Theta}^2)^{1/2}$, were in agreement with (4-2) for $N(\Theta)d\Theta$ for angles Θ in this range; but the angular distribution of the small number of particles scattered at larger angles was in marked disagreement with (4-2). It was found, for example, that the fraction of α 's scattered at angles greater than 90° , $N(\Theta > 90^\circ)/I$, was about 10^{-4} . What does (4-2) predict?

► We have

$$\frac{N(\Theta > 90^\circ)}{I} = \frac{\int_{90^\circ}^{180^\circ} N(\Theta)d\Theta}{I} = e^{-(90^\circ)^2} = 10^{-3500}$$

a strikingly different result than the experiment value of 10^{-4} .

In general the number of scattered α particles was observed to be *very* much larger than the predicted number for all scattering angles greater than a few degrees. ◀

The existence of a small, but nonzero probability for scattering at large angles could not be explained at all in terms of Thomson's model of the atom, which basically involves *small* angle scattering from *many* atoms. To scientists accustomed to thinking in terms of this model it came as a great surprise that some α particles were deflected through very large angles, up to 180° . In Rutherford's words: "It was quite the most incredible event that ever happened to me in my life. It was as incredible as if you fired a 15-inch shell at a piece of tissue paper and it came back and hit you."

Experiments using foils of various thicknesses showed that the number of large angle scatterings was proportional to N , the number of atoms traversed by the α particle. This is just the dependence on N that would arise if there were a small probability that an α particle could be scattered through a *large angle* in traversing a *single atom*. That cannot happen in Thomson's model of the atom, and this led Rutherford in 1911 to propose a new model.

4-2 RUTHERFORD'S MODEL

In Rutherford's model of the structure of the atom, all the positive charge of the atom, and consequently essentially all its mass, are assumed to be concentrated in a small region in the center called the *nucleus*. If the dimensions of the nucleus are small enough, an α particle passing very near it can be scattered by a strong Coulomb repulsion through a large angle in the traversal of a *single atom*. If, instead of using $r' = 10^{-10}$ m for the radius of the positive charge distribution of the Thomson atom, which leads to a maximum deflection angle $\theta \approx 10^{-4}$ rad, we ask what the radius r' of a nucleus should be to obtain $\theta \approx 1$ rad, say, we find $r' = 10^{-14}$ m. This, as we shall see, turns out to be a good estimate of the radius of the atomic nucleus.

Rutherford made a detailed calculation of the angular distribution to be expected for the scattering of α particles from atoms of the type proposed in his model. The calculation was concerned only with scattering at angles greater than several degrees. Hence, scattering due to atomic electrons can be ignored. The scattering is then due to the repulsive Coulomb force acting between the positively charged α particle and the positively charged nucleus. Furthermore, the calculation considered only the scattering from heavy atoms, to permit the assumption that the mass of the nucleus is so large compared to that of the α particle that the nucleus does not recoil appreciably (remains fixed in space) during the scattering process. It was also assumed that the α particle does not actually penetrate the nuclear region, so that the particle and the nucleus (both assumed to be spherical) act like point charges as far as the Coulomb force is concerned. We shall see later that all these assumptions are quite valid except for the scattering of α particles from the lighter nuclei, and we can correct for the finite nuclear mass in such cases. The calculation, finally, uses non-relativistic mechanics, since $v/c \approx 1/20$.

Figure 4-4 illustrates the scattering of an α particle, of charge $+ze$ and mass M , in passing near a nucleus of charge $+Ze$. The nucleus is fixed at the origin of the coordinate system. When the particle is very far from the nucleus, the Coulomb force on it is negligible so that the particle approaches the nucleus along a straight line with constant speed v . After the scattering, the particle will move off finally along a straight line again with constant speed v' . The position of the particle relative to the nucleus is specified by the radial coordinate r and the polar angle φ , with the latter measured from an axis drawn parallel to the initial trajectory line. The perpendicular distance from that axis to the line of initial motion is called the *impact parameter*, specified by b . The scattering angle θ is just the angle between the axis and a line drawn through the origin parallel to the line of final motion; the perpendicular distance between these two lines is b' .

Example 4-3. Show that $v = v'$ and $b = b'$.

► The force acting on the particle, being a Coulomb force, is always in the radial direction. Hence, the angular momentum of the particle about the origin has a constant value, L . Specifically then, the initial angular momentum is equal to the final angular momentum, or

$$Mvb = Mv'b' = L$$

Of course, the kinetic energy of the particle does not remain constant during the scattering, but the initial kinetic energy must be equal to the final kinetic energy since the nucleus is

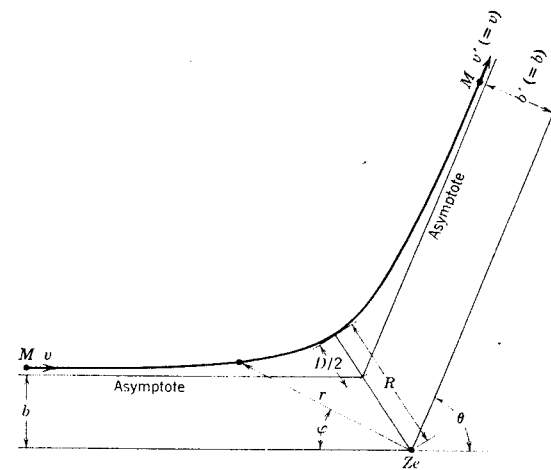


Figure 4-4 The hyperbolic Rutherford trajectory, showing the polar coordinates r, φ and the parameters b, D . These two parameters completely determine the trajectory, in particular the scattering angle θ and the distance of closest approach R . The nuclear point charge Ze lies at a focus of the branch of the hyperbola.

assumed to remain stationary. Thus

$$\frac{1}{2} Mv^2 = \frac{1}{2} Mv'^2$$

Therefore, $v = v'$ and so from the previous equation $b = b'$, as drawn in Figure 4-4. ◀

By a straightforward calculation of classical mechanics, using the repulsive Coulomb force $(1/4\pi\epsilon_0)(zZe^2/r^2)$, we can obtain the following equation for the trajectory of the α particle (see Appendix E for a derivation)

$$\frac{1}{r} = \frac{1}{b} \sin \varphi + \frac{D}{2b^2} (\cos \varphi - 1) \quad (4-3)$$

the equation of a hyperbola in polar coordinates. Here D is a constant, defined by

$$D \equiv \frac{1}{4\pi\epsilon_0} \frac{zZe^2}{Mv^2/2} \quad (4-4)$$

It is a convenient parameter equal to the *distance of closest approach* to the nucleus in a *head-on collision* ($b = 0$), since D is the distance at which the potential energy $(1/4\pi\epsilon_0)(zZe^2/D)$ is equal to the initial kinetic energy $Mv^2/2$ (simply equate the two and solve for D). At this point the particle would come to a stop and then reverse its direction of motion. The scattering angle θ follows from (4-3) by finding the value of φ as $r \rightarrow \infty$ and setting $\theta = \pi - \varphi$. In this way we find

$$\cot \frac{\theta}{2} = \frac{2b}{D} \quad (4-5)$$

Example 4-4. Evaluate R , the distance of closest approach of the particle to the center of the nucleus (the origin in Figure 4-4).

► The radial coordinate r will equal R when the polar angle is $\varphi = (\pi - \theta)/2$. Evaluating (4-3) for this angle, we get

$$\frac{1}{R} = \frac{1}{b} \sin \left(\frac{\pi - \theta}{2} \right) + \frac{D}{2b^2} \left[\cos \left(\frac{\pi - \theta}{2} \right) - 1 \right]$$

Now, from (4-5) we can put

$$b = \frac{D}{2} \cot \frac{\theta}{2} = \frac{D}{2} \tan \left(\frac{\pi - \theta}{2} \right)$$

and, after some manipulation, obtain

$$R = \frac{D}{2} \left[1 + \frac{1}{\cos \left(\frac{\pi - \theta}{2} \right)} \right]$$

or

$$R = \frac{D}{2} \left[1 + \frac{1}{\sin (\theta/2)} \right] \quad (4-6)$$

This result can be checked physically. Note that as $\theta \rightarrow \pi$, corresponding to $b = 0$ or a head-on collision, $R \rightarrow D$, the distance of closest approach. Also, as $\theta \rightarrow 0$, corresponding to no deflection at all, both b and R go to infinity, as would be expected. ◀

From (4-5) we see that, in the scattering of an α particle by a single nucleus, if the impact parameter is in the range b to $b + db$ then the scattering angle is in the range θ to $\theta + d\theta$, where the relation between b and θ is given by the equation. This is illustrated in Figure 4-5. The problem of calculating the number $N(\Theta)d\Theta$ of α particles scattered into the angular range Θ to $\Theta + d\Theta$ in traversing the entire foil is therefore equivalent to the problem of calculating the number which are incident, with impact parameter from b to $b + db$, upon the nuclei in the foil. As we show in the following example, the result is

$$N(\Theta)d\Theta = \left(\frac{1}{4\pi\epsilon_0} \right)^2 \left(\frac{zZe^2}{2Mr^2} \right)^2 \frac{I\rho t 2\pi \sin \Theta d\Theta}{\sin^4 (\Theta/2)} \quad (4-7)$$

where I is the number of α particles incident on a foil of thickness t cm containing ρ nuclei per cubic centimeter.

Example 4-5. Verify (4-7).

► Consider a segment of the foil with a cross-sectional area of 1 cm^2 , as shown in Figure 4-6. A ring, of inner radius b and outer radius $b + db$, is drawn around an incident axis passing through each nucleus, the area of each ring being $2\pi b db$. The number of such rings in this segment of the foil is ρt . The probability that an α particle will pass through one of these rings, $P(b)db$, is equal to the total area obscured by the rings, as seen by the incident α particles, divided by the total area of the segment. We assume the foil to be thin enough that we can ignore overlapping of rings from different nuclei. The process involves *single scattering* and the probability for appreciable scattering by more than one nucleus is very low. Hence

$$P(b)db = \rho t 2\pi b db$$

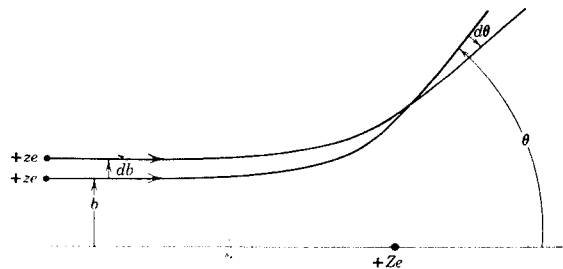


Figure 4-5 The relation between the impact parameter b and the scattering angle θ . As b increases (less close nuclear approach) the angle θ decreases (smaller scattering angle). The α particles with impact parameters between b and $b + db$ are scattered into the angular range between θ and $\theta + d\theta$.

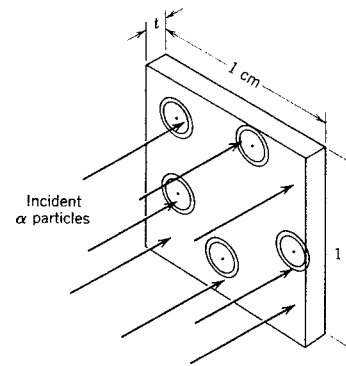


Figure 4-6 A beam of α particles incident on a foil of 1 cm^2 area and thickness t cm. The rings, which are purely geometrical constructs and not anything physical, are centered on nuclei. Actually there are enormously many more rings than shown and the rings are very much smaller than shown.

but $b = (D/2) \cot (\theta/2)$ so that

$$db = - \frac{D}{2} \frac{d\theta/2}{\sin^2 (\theta/2)}$$

and

$$b db = - \frac{D^2 \cos (\theta/2) d\theta}{8 \sin^3 (\theta/2)} = - \frac{D^2 \sin \theta d\theta}{16 \sin^4 (\theta/2)}$$

Thus

$$P(b)db = - \frac{\pi}{8} \rho t D^2 \sin \theta \frac{d\theta}{\sin^4 (\theta/2)}$$

But $-P(b)db$ is equal to the probability that the incident particles will be scattered into the angular range θ to $\theta + d\theta$. The minus sign arises from the fact that a decrease in b , i.e., $-db$, corresponds to an increase in θ , i.e., $+d\theta$. Using our earlier notation Θ for the scattering angle in passing through the entire foil, this is

$$\frac{N(\Theta)d\Theta}{I} = -P(b)db = \frac{\pi}{8} \rho t D^2 \frac{\sin \Theta d\Theta}{\sin^4 (\Theta/2)}$$

Finally, with $D = (1/4\pi\epsilon_0)zZe^2/(Mr^2/2)$, we obtain (4-7). ◀

If we compare the Rutherford atom result, (4-7), to the Thomson atom result, (4-2), we see that although the angular factor decreases rapidly with increasing angle in both, the decrease is very much less rapid for Rutherford's prediction. Large angle scattering is very much more probable in single scattering from a nuclear atom than in multiple small angle scattering from a plum pudding atom. Detailed experimental tests of (4-7) were performed within a few months of its derivation by Geiger and Marsden, with the following results:

1. The angular dependence was tested, using foils of Ag and Au, over the angular range 5° to 150° . Although $N(\Theta)d\Theta$ varies by a factor of about 10^5 over this range, the experimental data remained proportional to the theoretical angular distribution to within a few percent.

2. The quantity $N(\Theta)d\Theta$ was found indeed to be proportional to the thickness t of the foil for a range of about 10 in thickness for all the elements investigated.

3. Equation (4-7) predicts that the number of scattered α 's will be inversely proportional to the square of their kinetic energy, $Mr^2/2$. This was tested by using α particles from several different radioactive sources and the predicted energy dependence was confirmed experimentally over an available energy variation of about a factor of 3.

4. Finally, the equation predicts $N(\Theta)d\Theta$ to be proportional to $(Ze)^2$, the square of the nuclear charge. At the time Z was not known for the various atoms. Assuming

(4-7) to be valid, the experiment was used to determine Z and it was found that Z was equal to the chemical *atomic number* of the target atoms. This implied that the first atom, H, in the periodic table contains one electron, the second atom, He, contains two electrons, the third atom, Li, contains three, etc., since Z is also the number of electrons in the neutral atom. This result was soon independently confirmed by x-ray techniques that will be discussed in Chapter 9.

Rutherford, his model now confirmed, was able to put limits on the size of the nucleus. The distance of closest approach, D , is the smallest value that R takes on, which is R at $\Theta = 180^\circ$. Hence

$$R_{180^\circ} = D = \frac{1}{4\pi\epsilon_0} \frac{zZe^2}{Mv^2/2}$$

The nucleus radius must be no larger than D because the results are based on the assumption that the force acting on the α particle is always strictly a Coulomb force between two point charges. This assumption would not be true if the particle penetrated the nuclear region at its distance of closest approach. The previous equation shows that R_{180° decreases as Z decreases. The question arises: How much can R_{180° decrease before R_{180° is less than the nuclear radius? Departures from the predicted Rutherford scattering were actually observed from the very light (low Z) nuclei. Part of this was due to a violation, for the very light nuclei, of the assumption that the nuclear mass is large compared to the alpha particle mass; however, deviations remained even after the finite nuclear mass was taken into account in the theory. This suggests that penetration of the nucleus occurs in these cases thereby altering the predicted scattering. Hence, the nuclear radius can be defined as the value of R at the limiting scattering angle, or limiting incident energy, at which deviations from Rutherford scattering set in. In Figure 4-7, for example, we show data from Rutherford's group for the scattering of α particles, of various energies, at a fixed large angle from an Al foil. The ordinate is the ratio of the observed number of scattered particles to the number predicted by the Rutherford theory (corrected for the finite nuclear mass). The abscissa is the distance of closest approach calculated from (4-6). These data imply that the radius of the Al nucleus is about 10^{-14} m = 10 F. (The unit of distance used in nuclear physics is the *fermi*, which equals 10^{-15} m. Note that 1 F = 10^{-5} Å, where Å, the angstrom, is the unit used in atomic physics.)

The Rutherford scattering formula, (4-7), is usually expressed in terms of a *differential cross section* $d\sigma/d\Omega$. This quantity is defined so that the number dN of α particles scattered into a solid angle $d\Omega$ at scattering angle Θ is

$$dN = \frac{d\sigma}{d\Omega} \ln d\Omega \quad (4-8)$$

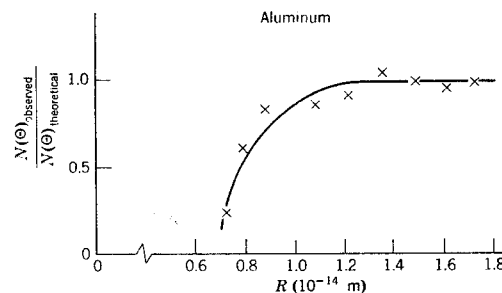


Figure 4-7 Some data obtained in the scattering of α particles from a radioactive source by aluminum. The abscissa is the distance of closest approach to the nuclear center.

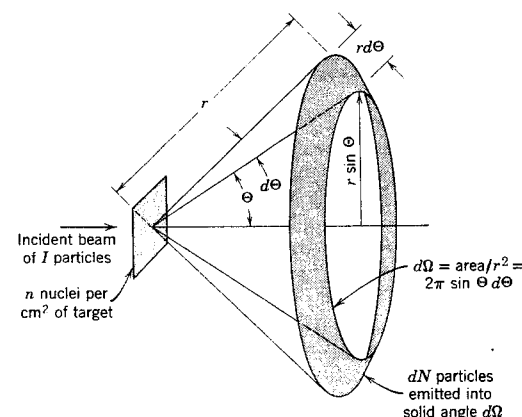


Figure 4-8 Illustrating the definition of the differential cross section $d\sigma/d\Omega$. If the target is thin enough for an incident particle to have negligible chance of interacting with more than one nucleus while passing through the target, then $dN = (d\sigma/d\Omega) \ln d\Omega$.

if I α particles are incident on a target foil containing n nuclei per square centimeter. The definition is analogous to the definition of a cross section σ in (2-18)

$$N = \sigma I n$$

It is illustrated in Figure 4-8. The *solid angle* $d\Omega$, which is essentially a two-dimensional angular range, is measured numerically by the area which the angular range includes on a sphere of unit radius centered where the scatterings occur. For Rutherford scattering, which is symmetric about the axis of the incident beam, we are interested in the solid angle $d\Omega$ corresponding to all events in which the scattering angle lies in the range $d\Theta$ at Θ . As is shown in the figure

$$d\Omega = 2\pi \sin \Theta d\Theta$$

Using this in (4-7), writing $N(\Theta)d\Theta$ in that equation as dN , and also writing the term ρt appearing there as n , we immediately obtain

$$dN = \left(\frac{1}{4\pi\epsilon_0} \right)^2 \left(\frac{zZe^2}{2Mv^2} \right)^2 \frac{1}{\sin^4(\Theta/2)} \ln d\Omega$$

Comparison with the definition of (4-8) then shows that the *Rutherford scattering differential cross section* is

$$\frac{d\sigma}{d\Omega} = \left(\frac{1}{4\pi\epsilon_0} \right)^2 \left(\frac{zZe^2}{2Mv^2} \right)^2 \frac{1}{\sin^4(\Theta/2)} \quad (4-9)$$

4-3 THE STABILITY OF THE NUCLEAR ATOM

The detailed experimental verification of the predictions of Rutherford's nuclear model of the atom left little room for doubt concerning the validity of the model. At the center of the atom is a nucleus whose mass is approximately that of the entire atom and whose charge is equal to the atomic number Z times e ; around this nucleus there exist Z electrons, neutralizing the atom as a whole. But serious questions emerge about the *stability* of such an atom. If we assume, for example, that the electrons in the atom are stationary, there exists no stable arrangement of the electrons which would prevent the electrons from falling into the nucleus under the influence of its Coulomb attraction. We cannot allow the atom to collapse (back to a nuclear-sized plum pudding) because then its radius would be of the order of a

nuclear radius, which is four orders of magnitude smaller than diverse experiments show the radius of the atom to be.

At first glance it seems that we can simply allow the electrons to circulate about the nucleus in orbits similar to the orbits of the planets circulating about the sun. Such a system can be stable mechanically, as is the solar system. A serious difficulty arises, however, in trying to carry over this idea from the planetary system to the atomic system. The problem is that the charged electrons would be constantly accelerating in their motion around the nucleus and, according to classical electromagnetic theory, all accelerating charged bodies radiate energy in the form of electromagnetic radiation (see Appendix B). The energy would be emitted at the expense of the mechanical energy of the electron, and the electron would spiral into the nucleus. Again we have an atom which would rapidly collapse to nuclear dimensions. (For an atom of diameter 10^{-10} m the time of collapse can be computed to be $\approx 10^{-12}$ sec!) Furthermore, the continuous spectrum of the radiation that would be emitted in this process is not in agreement with the discrete spectrum which is known to be emitted by atoms.

This difficult problem of the stability of atoms actually led to a simple model of atomic structure. A key feature of this very successful model, proposed by Niels Bohr in 1913, was the prediction of the spectrum of radiation emitted by certain atoms. Hence, it is appropriate at this point to describe some of the principal features of such spectra.

4-4 ATOMIC SPECTRA

A typical apparatus used in the measurement of atomic spectra is indicated in Figure 4-9. The source consists of an electric discharge passing through a region containing a monatomic gas. Owing to collisions with electrons, and with each other, some of the atoms in the discharge are put into a state in which their total energy is greater than it is in a normal atom. In returning to their normal energy state, the atoms give up their excess energy by emitting electromagnetic radiation. The radiation is collimated by the slit and then it passes through a prism (or diffraction grating) for better resolution) where it is broken up into its wavelength spectrum which is recorded on the photographic plate.

The nature of the observed spectra is indicated on the photographic plate. In contrast to the continuous spectrum of electromagnetic radiation emitted, for instance, from the surface of solids at high temperature, the electromagnetic radiation emitted

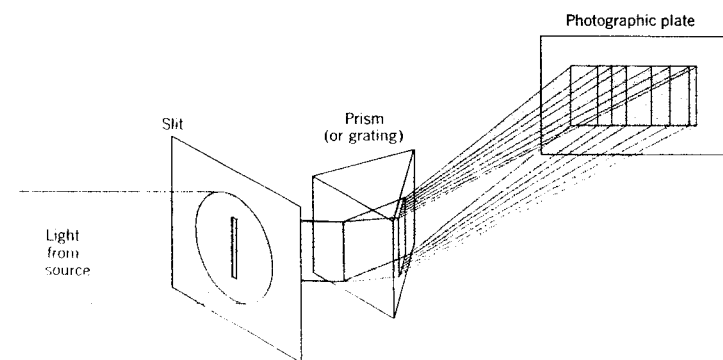


Figure 4-9 Schematic of an apparatus used to measure atomic spectra

by free atoms is concentrated at a number of discrete wavelengths. Each of these wavelength components is called a *line* because of the line (image of the slit) which it produces on the photographic plate. Investigation of the spectra emitted from different kinds of atoms shows that each kind of atoms has its own characteristic spectrum, i.e., a characteristic set of wavelengths at which the lines of the spectrum are found. This feature is of greatest practical importance because it makes *spectroscopy* a very useful addition to the usual techniques of chemical analysis. Chiefly for this reason much effort was devoted to the accurate measurement of atomic spectra, and, in fact, much effort was needed because the spectra consist of many hundreds of lines and in general are very complicated.

However, the spectrum of hydrogen is relatively simple. This is perhaps not surprising since hydrogen, which contains just one electron, is itself the simplest atom. Most of the universe consists of isolated hydrogen atoms so that the hydrogen spectrum is of considerable practical interest. There are historical and theoretical reasons as well for studying it, as will become apparent later. Figure 4-10 shows that part of the atomic hydrogen spectrum which falls approximately within the wavelength range of visible light. We see that the spacing, in wavelengths, between adjacent lines of the spectrum continuously decreases with decreasing wavelength of the lines, so that the *series of lines* converges to the so-called *series limit* at 3645.6 Å. The short wavelength lines, including the series limit, are hard to observe experimentally because of their close spacing and because they are in the ultraviolet.

The obvious regularity of the H spectrum tempted several people to look for an empirical formula which would represent the wavelength of the lines. Such a formula was discovered in 1885 by Balmer. He found that the simple equation

$$\lambda = 3646 \frac{n^2}{n^2 - 4} \quad (\text{in } \text{\AA} \text{ units})$$

where $n = 3$ for H_α , $n = 4$ for H_β , $n = 5$ for H_γ , etc., was able to predict the wavelength of the first nine lines of the series, which were all that were known at the time, to better than one part in 1000. This discovery initiated a search for similar empirical formulas that would apply to series of lines which can sometimes be identified in the complicated distribution of lines that constitute the spectra of other elements. Most of this work was done around 1890 by Rydberg, who found it convenient to deal with the reciprocal of the wavelength of the lines, instead of their wavelength. In terms of reciprocal wavelength κ the *Balmer formula* can be written

$$\kappa = 1/\lambda = R_H(1/2^2 - 1/n^2) \quad n = 3, 4, 5, \dots \quad (4-10)$$

where R_H is the so-called *Rydberg constant* for hydrogen. From recent spectroscopic

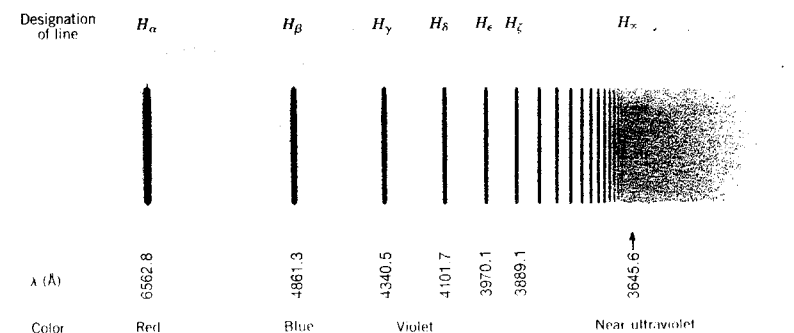


Figure 4-10 A photograph of the visible part of the hydrogen spectrum (Spectrum from W. Finkelburg, *Structure of Matter*, Springer-Verlag, Heidelberg, 1964)

Table 4-1 The Hydrogen Series

Names	Wavelength Ranges	Formulas
Lyman	Ultraviolet	$\kappa = R_H \left(\frac{1}{1^2} - \frac{1}{n^2} \right) \quad n = 2, 3, 4, \dots$
Balmer	Near ultraviolet and visible	$\kappa = R_H \left(\frac{1}{2^2} - \frac{1}{n^2} \right) \quad n = 3, 4, 5, \dots$
Paschen	Infrared	$\kappa = R_H \left(\frac{1}{3^2} - \frac{1}{n^2} \right) \quad n = 4, 5, 6, \dots$
Brackett	Infrared	$\kappa = R_H \left(\frac{1}{4^2} - \frac{1}{n^2} \right) \quad n = 5, 6, 7, \dots$
Pfund	Infrared	$\kappa = R_H \left(\frac{1}{5^2} - \frac{1}{n^2} \right) \quad n = 6, 7, 8, \dots$

data, its value is known to be

$$R_H = 10967757.6 \pm 1.2 \text{ m}^{-1}$$

This indicates the accuracy possible in spectroscopic measurements.

Formulas of this type were found for a number of series. For instance, we now know of the existence of five series of lines in the hydrogen spectrum, as shown in Table 4-1.

For alkali element atoms (Li, Na, K, ...) the series formulas are of the same general structure. That is

$$\kappa = \frac{1}{\lambda} = R \left[\frac{1}{(m-a)^2} - \frac{1}{(n-b)^2} \right] \quad (4-11)$$

where R is the Rydberg constant for the particular element, a and b are constants for the particular series, m is an integer which is fixed for the particular series, and n is a variable integer. To within about 0.05% the Rydberg constant has the same value for all elements, although it does show a very slight systematic increase with increasing atomic weight.

We have been discussing the *emission spectrum* of an atom. A closely related property is the *absorption spectrum*. This may be measured with apparatus similar to that shown in Figure 4-9 except that a source emitting a continuous spectrum is used and a glass-walled cell, containing the monatomic gas to be investigated, is inserted somewhere between the source and the prism. After exposure and development, the photographic plate is found to be darkened everywhere except for a number of unexposed lines. These lines represent a set of discrete wavelength components which were missing from the otherwise continuous spectrum incident upon the prism, and which must have been absorbed by the atoms in the gas cell. It is observed that for every line in the absorption spectrum of an element there is a corresponding (same wavelength) line in its emission spectrum; however, the reverse is not true. Only certain emission lines show up in the absorption spectrum. For hydrogen gas, normally only lines corresponding to the Lyman series appear in the absorption spectrum; but, when the gas is at very high temperatures, e.g., at the surface of a star, lines corresponding to the Balmer series are found.

4-5 BOHR'S POSTULATES

All these features of atomic spectra, and many more which we have not discussed, must be explained by any successful model of atomic structure. Furthermore, the very great precision of spectroscopic measurements imposes severe requirements on the

accuracy with which such a model must be able to predict the quantitative features of the spectra.

Nevertheless, in 1913 Niels Bohr developed a model which was in accurate quantitative agreement with certain of the spectroscopic data (e.g., the hydrogen spectrum). It had the additional attraction that the mathematics involved was very easy to understand. Although the student has probably seen something of Bohr's model in studying elementary physics, or chemistry, we shall consider it in detail here in order to obtain various results that we shall want to make comparisons with elsewhere in this book, and also in order to take a careful look at the rather confusing postulates on which the model is based. These postulates are:

1. *An electron in an atom moves in a circular orbit about the nucleus under the influence of the Coulomb attraction between the electron and the nucleus, obeying the laws of classical mechanics.*
2. *Instead of the infinity of orbits which would be possible in classical mechanics, it is only possible for an electron to move in an orbit for which its orbital angular momentum L is an integral multiple of \hbar , Planck's constant divided by 2π .*
3. *Despite the fact that it is constantly accelerating, an electron moving in such an allowed orbit does not radiate electromagnetic energy. Thus, its total energy E remains constant.*
4. *Electromagnetic radiation is emitted if an electron, initially moving in an orbit of total energy E_i , discontinuously changes its motion so that it moves in an orbit of total energy E_f . The frequency of the emitted radiation ν is equal to the quantity $(E_i - E_f)$ divided by Planck's constant h .*

The first postulate bases Bohr's model on the existence of the atomic nucleus. The second postulate introduces quantization. Note the difference, however, between Bohr's quantization of the *orbital angular momentum* of an atomic electron moving under the influence of an *inverse square (Coulomb) force*

$$L = n\hbar \quad n = 1, 2, 3, \dots \quad (4-12)$$

and Planck's quantization of the *energy* of a particle, such as an electron, executing simple harmonic motion under the influence of a *harmonic restoring force*: $E = nh\nu$, $n = 0, 1, 2, \dots$. We shall see in the next section that the quantization of the orbital angular momentum of the atomic electron does lead to the quantization of its total energy, but with an energy quantization equation which is different from Planck's equation. The third postulate removes the problem of the stability of an electron moving in a circular orbit, due to the emission of the electromagnetic radiation required of the electron by classical theory, by simply postulating that this particular feature of the classical theory is not valid for the case of an atomic electron. The postulate was based on the fact that *atoms are observed by experiment to be stable*—even though this is not predicted by the classical theory. The fourth postulate

$$\nu = \frac{E_i - E_f}{h} \quad (4-13)$$

is really just Einstein's postulate that the frequency of a photon of electromagnetic radiation is equal to the energy carried by the photon divided by Planck's constant.

These postulates do a thorough job of mixing classical and nonclassical physics. The electron moving in a circular orbit is assumed to obey classical mechanics, and yet the nonclassical idea of quantization of orbital angular momentum is included. The electron is assumed to obey one feature of classical electromagnetic theory (Coulomb's law), and yet not to obey another feature (emission of radiation by an accelerated charged body). However, we should not be surprised if the laws of classical physics, which are based on our experience with macroscopic systems, are not completely valid when dealing with microscopic systems such as the atom.

4-6 BOHR'S MODEL

The justification of Bohr's postulates, or of any set of postulates, can be found only by comparing the predictions that can be derived from the postulates with the results of experiment. In this section we derive some of these predictions and compare them with the data of Section 4-4.

Consider an atom consisting of a nucleus of charge $+Ze$ and mass M , and a single electron of charge $-e$ and mass m . For a neutral hydrogen atom $Z = 1$, for a singly ionized helium atom $Z = 2$, for a doubly ionized lithium atom $Z = 3$, etc. We assume that the electron revolves in a circular orbit about the nucleus. Initially we suppose the mass of the electron to be completely negligible compared to the mass of the nucleus, and consequently assume that the nucleus remains fixed in space. The condition of mechanical stability of the electron is

$$\frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r^2} = m \frac{v^2}{r} \quad (4-14)$$

where v is the speed of the electron in its orbit, and r is the radius of the orbit. The left side of this equation is the Coulomb force acting on the electron, and the right side is ma , where a is the centripetal acceleration keeping the electron in its circular orbit. Now, the orbital angular momentum of the electron, $L = mvr$, must be a constant, because the force acting on the electron is entirely in the radial direction. Applying the quantization condition, (4-12), to L , we have

$$mvr = n\hbar \quad n = 1, 2, 3, \dots \quad (4-15)$$

Solving for v and substituting into (4-14), we obtain

$$Ze^2 = 4\pi\epsilon_0 m v^2 r = 4\pi\epsilon_0 m r \left(\frac{n\hbar}{mr} \right)^2 = 4\pi\epsilon_0 \frac{n^2 \hbar^2}{mr}$$

so

$$r = 4\pi\epsilon_0 \frac{n^2 \hbar^2}{mZe^2} \quad n = 1, 2, 3, \dots \quad (4-16)$$

and

$$v = \frac{n\hbar}{mr} = \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{n\hbar} \quad n = 1, 2, 3, \dots \quad (4-17)$$

The application of the angular momentum quantization condition has restricted the possible circular orbits to those of radii given by (4-16). Note that these radii are proportional to the square of the *quantum number* n . If we evaluate the radius of the smallest orbit ($n = 1$) for a hydrogen atom ($Z = 1$) by inserting the known values of h , m , and e , we obtain $r = 5.3 \times 10^{-11} \text{ m} \approx 0.5 \text{ \AA}$. We shall show later that the electron has its minimum total energy when in the orbit corresponding to $n = 1$. Consequently we may interpret the radius of this orbit as a measure of the radius of a hydrogen atom in its normal state. It is in good agreement with the estimate, mentioned previously, that the order of magnitude of an atomic radius is 1 \AA . Hence, Bohr's postulates predict a reasonable size for the atom. Evaluating the orbital velocity of an electron in the smallest orbit of a hydrogen atom from (4-17), we find $v = 2.2 \times 10^6 \text{ m/sec}$. It is apparent from the equation that this is the largest velocity possible for a hydrogen atom electron. The fact that this velocity is less than 1% of the velocity of light is the justification for using classical mechanics instead of relativistic mechanics in the Bohr model. On the other hand, (4-17) shows that for large values of Z the electron velocity becomes relativistic; the model could not be applied in such cases. That equation also makes it apparent why Bohr could not allow the quantum number n ever to assume the value $n = 0$, as it may in Planck's quantization equation.

Next we calculate the total energy of an atomic electron moving in one of the allowed orbits. Let us define the potential energy to be zero when the electron is

infinitely distant from the nucleus. Then the potential energy V at any finite distance r can be obtained by integrating the work that would be done by the Coulomb force acting from r to ∞ . Thus

$$V = - \int_r^\infty \frac{Ze^2}{4\pi\epsilon_0 r^2} dr = - \frac{Ze^2}{4\pi\epsilon_0 r}$$

The potential energy is negative because the Coulomb force is attractive; it takes work to move the electron from r to infinity against this force. The kinetic energy of the electron, K , can be evaluated, with the aid of (4-14), to be

$$K = \frac{1}{2} mv^2 = \frac{Ze^2}{4\pi\epsilon_0 2r}$$

The total energy of the electron, E , is then

$$E = K + V = - \frac{Ze^2}{4\pi\epsilon_0 2r} = -K$$

Using (4-16) for r in the preceding equation, we have

$$E = - \frac{mZ^2 e^4}{(4\pi\epsilon_0)^2 2\hbar^2} \frac{1}{n^2} \quad n = 1, 2, 3, \dots \quad (4-18)$$

We see that the quantization of the orbital angular momentum of the electron leads to a quantization of its total energy.

The information contained in (4-18) is presented as an energy-level diagram in Figure 4-11. The energy of each level, as evaluated from (4-18), is shown on the left, in terms of joules and electron volts, and the quantum number of the level is shown on the right. The diagram is so constructed that the distance from any level to the level of zero energy is proportional to the energy of that level. Note that the lowest (most negative) allowed value of total energy occurs for the smallest quantum number $n = 1$. As n increases, the total energy of the quantum state becomes less negative, with E approaching zero as n approaches infinity. Since the state of lowest total energy is, of course, the most stable state for the electron, we see that the normal state of the electron in a one-electron atom is the state for which $n = 1$.

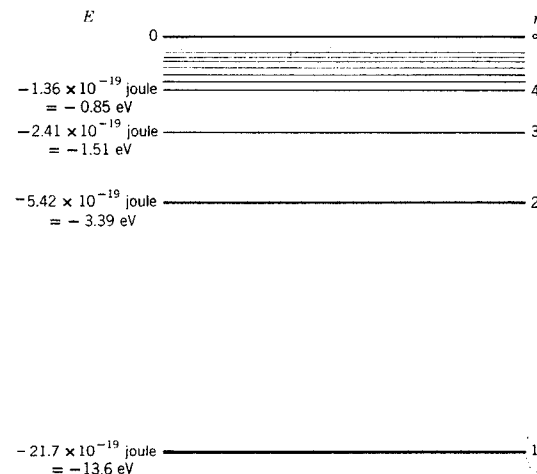


Figure 4-11 An energy-level diagram for the hydrogen atom.

Example 4-6. Calculate the binding energy of the hydrogen atom (the energy binding the electron to the nucleus) from (4-18).

► The binding energy is numerically equal to the energy of the lowest state in Figure 4-11, corresponding to $n = 1$ in (4-18). This yields, with $Z = 1$

$$\begin{aligned} E &= -\left(\frac{1}{4\pi\epsilon_0}\right) \frac{me^4}{2h^2} \\ &= -\frac{(9.0 \times 10^9 \text{ nt-m}^2/\text{coul}^2)^2 \times 9.11 \times 10^{-31} \text{ kg} \times (1.60 \times 10^{-19} \text{ coul})^4}{2 \times (1.05 \times 10^{-34} \text{ joule-sec})^2} \\ &= -2.17 \times 10^{-18} \text{ joule} = -13.6 \text{ eV} \end{aligned}$$

which agrees very well with the experimentally observed binding energy for hydrogen. ◀

Next we calculate the frequency ν of the electromagnetic radiation emitted when the electron makes a transition from the quantum state n_i to the quantum state n_f , that is, when an electron initially moving in an orbit characterized by the quantum number n_i discontinuously changes its motion so that it moves in an orbit characterized by quantum number n_f . Using Bohr's fourth postulate (4-13), and (4-18), we have

$$\nu = \frac{E_i - E_f}{h} = + \left(\frac{1}{4\pi\epsilon_0}\right)^2 \frac{mZ^2e^4}{4\pi h^3} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

In terms of the reciprocal wavelength $\kappa = 1/\lambda = \nu/c$, this is

$$\kappa = \left(\frac{1}{4\pi\epsilon_0}\right)^2 \frac{me^4}{4\pi h^3 c} Z^2 \left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

or

$$\kappa = R_\infty Z^2 \left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) \quad \text{where } R_\infty \equiv \left(\frac{1}{4\pi\epsilon_0}\right)^2 \frac{me^4}{4\pi h^3 c} \quad (4-19)$$

and where n_i and n_f are integers.

The essential predictions of the Bohr model are contained in (4-18) and (4-19). Let us first discuss the emission of electromagnetic radiation by a one-electron Bohr atom in terms of these equations.

1. The normal state of the atom will be the state in which the electron has the lowest energy, i.e., the state $n = 1$. This is called the *ground state*. (Ground state means fundamental state, the term originating from the German word *grund*, meaning fundamental.)

2. In an electric discharge, or in some other process, the atom receives energy due to collisions, etc. This means that the electron must make a transition to a state of higher energy, or *excited state*, in which $n > 1$.

3. Obeying the common tendency of all physical systems, the atom will emit its excess energy and return to the ground state. This is accomplished by a series of transitions in which the electron drops to excited states of successively lower energy, finally reaching the ground state. In each transition electromagnetic radiation is emitted with a wavelength which depends on the energy lost by the electron, i.e., on the initial and final quantum numbers. In a typical case, the electron might be excited into state $n = 7$ and drop successively through the states $n = 4$ and $n = 2$ to the ground state $n = 1$. Three lines of the atomic spectrum are emitted with reciprocal wavelengths given by (4-19) for $n_i = 7$ and $n_f = 4$, $n_i = 4$ and $n_f = 2$, and $n_i = 2$ and $n_f = 1$.

4. In the very large number of excitation and deexcitation processes which take place during a measurement of an atomic spectrum, all possible transitions occur and the complete spectrum is emitted. The reciprocal wavelengths, or wavelengths, of the set of lines which constitute the spectrum are given by (4-19), where we allow

n_i and n_f to take on all possible integral values subject only to the restriction that $n_i > n_f$.

For hydrogen ($Z = 1$) let us consider the subset of spectral lines which arises from transitions in which $n_f = 2$. According to (4-19) the reciprocal wavelengths of these lines are given by

$$\kappa = R_\infty (1/n_f^2 - 1/n_i^2) \quad n_f = 2 \text{ and } n_i > n_f$$

or

$$\kappa = R_\infty (1/2^2 - 1/n^2) \quad n = 3, 4, 5, 6, \dots$$

This is identical with the series formula for the Balmer series of the hydrogen spectrum (4-10), if R_∞ is equal to R_H . According to the Bohr Model

$$R_\infty = \left(\frac{1}{4\pi\epsilon_0}\right)^2 \frac{me^4}{4\pi h^3 c}$$

Although the numerical values of some of the quantities entering into this equation were not very accurately known at the time, Bohr evaluated R_∞ in terms of these quantities and found that the resulting value was in quite good agreement with the experimental value of R_H . In the next section we shall make a detailed comparison, using recent data, between the experimental value of R_H and Bohr's prediction, and we shall show that the two agree almost perfectly.

According to the Bohr model, each of the five known series of the hydrogen spectrum arises from a subset of transitions in which the electron goes to a certain final quantum state n_f . For the Lyman series $n_f = 1$; for the Balmer series $n_f = 2$; for the Paschen series $n_f = 3$; for the Brackett series $n_f = 4$; and for the Pfund series $n_f = 5$. The first three of these series are conveniently illustrated in terms of the energy-level diagram of Figure 4-12. The transition giving rise to a particular line of a series is indicated in this diagram by an arrow going from the initial quantum state n_i to the final quantum state n_f . Only the arrows corresponding to the first few lines of each series and to the series limit are shown. Since the distance between any two energy levels in such a diagram is proportional to the difference between the energy of the two levels, and since (4-13) states that the frequency ν (or reciprocal wavelength) is proportional to the energy difference, the length of any arrow is proportional to the frequency (or reciprocal wavelength) for the corresponding spectral line.

The wavelengths of the lines of all these series are fitted very accurately by (4-19) by using the appropriate value of n_f . This was a great triumph for Bohr's model. The success of the model was particularly impressive because the Lyman, Brackett, and Pfund series had not been discovered at the time the model was developed by Bohr. The existence of these series was predicted, and the series were soon found experimentally by the persons after whom they are named.

The model worked equally well when applied to the case of one-electron atoms with $Z = 2$, i.e., singly ionized helium atoms He^+ . Such atoms can be produced by passing a particularly violent electric discharge (a spark) through normal helium gas. They make their presence apparent by emitting a simpler spectrum than that emitted by normal helium atoms. In fact, the atomic spectrum of He^+ is exactly the same as the hydrogen spectrum except that the reciprocal wavelengths of all the lines are almost exactly four times as great. This is explained very easily, in terms of the Bohr model, by setting $Z^2 = 4$ in (4-19).

The properties of the absorption spectrum of one-electron atoms are also easy to understand in terms of the Bohr model. Since the atomic electron must have a total energy exactly equal to the energy of one of the allowed energy states, the atom can only absorb discrete amounts of energy from the incident electromagnetic radiation. This fact leads to the idea that we consider the incident radiation to be a beam of photons, and that only those photons can be absorbed whose frequency is given by

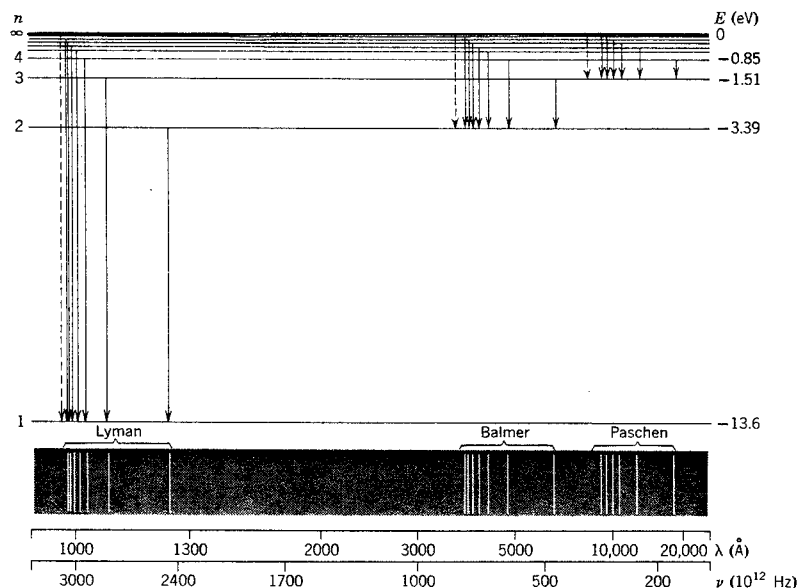


Figure 4-12 Top: The energy-level diagram for hydrogen with the quantum number n for each level and some of the transitions that appear in the spectrum. An infinite number of levels is crowded in between the levels marked $n=4$ and $n=\infty$. Bottom: The corresponding spectral lines for the three series indicated. Within each series the spectral lines follow a regular pattern, approaching the series limit at the shortwave end of the series. As drawn here, neither the wavelength nor frequency scale is linear, being chosen as they are merely for clarity of illustration. A linear wavelength scale would more nearly represent the actual appearance of the photographic plate obtained from a spectroscope. The Brackett and Pfund series, which are not shown, lie in the far infrared part of the spectrum.

$E = h\nu$, where E is one of the discrete amounts of energy which can be absorbed by the atom. The process of absorbing electromagnetic radiation is then just the inverse of the normal emission process, and the lines of the absorption spectrum will have exactly the same wavelengths as the lines of the emission spectrum. Normally the atom is always initially in the ground state $n=1$, so that only absorption processes from $n=1$ to $n>1$ can occur. Thus, only the absorption lines which correspond (for hydrogen) to the Lyman series will normally be observed. However, if the gas containing the absorbing atoms is at a very high temperature, then, owing to collisions, some of the atoms will initially be in the first excited state $n=2$, and absorption lines corresponding to the Balmer series will be observed.

Example 4-7. Estimate the temperature of a gas containing hydrogen atoms at which the Balmer series lines will be observed in the absorption spectrum.

► The Boltzmann probability distribution (see Appendix C) shows that the ratio of the number n_2 of atoms in the first excited state to the number n_1 of atoms in the ground state, in a large sample in thermal equilibrium at temperature T , is

$$\frac{n_2}{n_1} = \frac{e^{-E_2/kT}}{e^{-E_1/kT}}$$

where k is Boltzmann's constant, $k = 1.38 \times 10^{-23}$ joule/K $= 8.62 \times 10^{-5}$ eV/K. For hydrogen atoms the energies of these two states are given in the energy-level diagram of Fig-

ure 4-11: $E_1 = -13.6$ eV, $E_2 = -3.39$ eV. Hence

$$\frac{n_2}{n_1} = e^{(-3.39 + 13.6) \text{ eV} / (8.62 \times 10^{-5} \text{ eV/K}) T} = e^{-1.18 \times 10^5 \text{ K}/T}$$

Therefore, a significant fraction of the hydrogen atoms will initially be in the first excited state only when T is not too much smaller than 10^5 K; and only when they absorb from that state can they produce absorption lines of the Balmer series.

The situation is complicated by the fact that the $n=\infty$ level is not far above the $n=2$ level. This proximity makes the probability that hydrogen atoms will initially be ionized increase with increasing temperature about as rapidly as the probability that the atoms will initially be in their first excited state. But no absorption lines at all can be produced by initially ionized hydrogen atoms. Detailed calculations predict that the maximum amount of Balmer absorption should be observed when the temperature is about 10^4 K.

Balmer absorption lines are actually observed in the hydrogen gas of some stellar atmospheres. This gives us a way of estimating the temperature of the surface of a star. ◀

4-7 CORRECTION FOR FINITE NUCLEAR MASS

In the previous section we assumed the mass of the atomic nucleus to be infinitely large compared to the mass of the atomic electron, so that the nucleus remains fixed in space. This is a good approximation even for hydrogen, which contains the lightest nucleus, since the mass of that nucleus is about 2000 times larger than the electron mass. However, the spectroscopic data are so very accurate that before we make a detailed numerical comparison of these data with the Bohr model we must take into account the fact that the nuclear mass is actually finite. In such a case the electron and the nucleus move about their common center of mass. However, it is not difficult to show that in such a planetarylike system the electron moves relative to the nucleus as though the nucleus were fixed and the mass m of the electron were slightly reduced to the value μ , the *reduced mass* of the system. The equations of motion of the system are the same as those we have considered if we simply substitute μ for m , where

$$\mu = \frac{mM}{m+M} \quad (4-20)$$

is less than m by a factor $1/(1+m/M)$. Here M is the mass of the nucleus.

To handle this situation Bohr modified his second postulate to require that the total orbital angular momentum of the atom, L , is an integral multiple of Planck's constant divided by 2π . This is achieved by generalizing (4-15) to

$$\mu r v = n h \quad n = 1, 2, 3, \dots \quad (4-21)$$

Using μ instead of m in this equation takes into account the angular momentum of the nucleus as well as that of the electron. Making similar modifications to the rest of Bohr's derivation for the case of finite nuclear mass, we find that many of the equations are identical with those derived before, except that the electron mass m is replaced by the reduced mass μ . In particular, the formula for the reciprocal wavelengths of the spectral lines becomes

$$\kappa = R_M Z^2 \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \quad \text{where } R_M \equiv \frac{M}{m+M} R, \quad R = \frac{\mu}{m} R, \quad (4-22)$$

The quantity R_M is the *Rydberg constant for a nucleus of mass M* . As $M/m \rightarrow \infty$, it is apparent that $R_M \rightarrow R$, the Rydberg constant for an infinitely heavy nucleus which appears in (4-19). In general, the Rydberg constant R_M is less than R by the factor $1/(1+m/M)$. For the most extreme case of hydrogen, $M/m = 1836$ and R_M is less than R by about one part in 2000.

If we evaluate R_H from (4-22), using the currently accepted values of the quantities m , M , e , c , and h , we find $R_H = 10968100 \text{ m}^{-1}$. Comparing this with the experimental value of R_H given in Section 4-4, we see that the Bohr model, corrected for finite nuclear mass, agrees with the spectroscopic data to within three parts in 100,000!

Example 4-8. In Chapter 2 we spoke of the *positronium* "atom," consisting of a positron and an electron revolving about their common center of mass, which lies halfway between them.

(a) If such a system were a normal atom, how would its emission spectrum compare to that of the hydrogen atom?

► In this case the "nuclear" mass M is that of the positron, which equals m , the mass of the electron. Hence, the reduced mass (4-20) is

$$\mu = \frac{mM}{m+M} = \frac{m^2}{2m} = \frac{m}{2}$$

The corresponding Rydberg constant R_M is, according to (4-22)

$$R_M = \frac{m}{m+M} R_\infty = \frac{R_\infty}{2}$$

The energy states of the positronium atom then would be given by

$$E_{\text{positronium}} = -\frac{R_M hc Z^2}{n^2} = -\frac{R_\infty hc Z^2}{2n^2}$$

and the reciprocal wavelengths of the emitted spectral lines by

$$\kappa = \frac{1}{\lambda} = \frac{\nu}{c} = \frac{R_\infty}{2} Z^2 \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

The frequencies of the emitted lines would then be half, and the wavelengths double, that of a hydrogen atom (with infinitely heavy nucleus), Z being equal to one for positronium and for hydrogen.

(b) What would be the electron-positron separator, D , in the ground state orbit of positronium?

► In (4-16) we merely replace m by $\mu = m/2$ and we find

$$D_{\text{positronium}} = \frac{4\pi\epsilon_0 n^2 \hbar^2}{\mu Z e^2} = 2 \frac{4\pi\epsilon_0 n^2 \hbar^2}{m Z e^2} = 2r_{\text{hydrogen}}$$

Hence, for any quantum state n the distance of the electron from the "nucleus" is twice as great in the positronium atom as in the hydrogen atom (with infinitely heavy nucleus).

Example 4-9. A *muonic* atom contains a nucleus of charge Ze and a negative *muon*, μ^- , moving about it. The μ^- is an elementary particle with charge $-e$ and a mass that is 207 times as large as an electron mass.

(a) Calculate the muon-nucleus separation, D , of the first Bohr orbit of a muonic atom with $Z = 1$.

► The reduced mass of the system, with $m_\mu = 207m_e$ and $M = 1836m_e$, is, from (4-20)

$$\mu = \frac{207m_e \times 1836m_e}{207m_e + 1836m_e} = 186m_e$$

Then, from (4-16), with $n = 1$, $Z = 1$, and $m = 186m_e$, we obtain

$$D_1 = \frac{4\pi\epsilon_0 \hbar^2}{186m_e e^2} = \frac{1}{186} \times 5.3 \times 10^{-11} \text{ m} = 2.8 \times 10^{-13} \text{ m} = 2.8 \times 10^{-3} \text{ \AA}$$

Therefore the μ^- is much closer to the nuclear (proton) surface than is the electron in a hydrogen atom. It is this feature which makes such muonic atoms interesting, information about nuclear properties being revealed from their study.

(b) Calculate the binding energy of a muonic atom with $Z = 1$.

► From (4-18), with $Z = 1$, $n = 1$, and $m = \mu = 186m_e$, we have

$$E = -186 \frac{m_e e^4}{(4\pi\epsilon_0)^2 2\hbar^2} = -186 \times 13.6 \text{ eV} = -2530 \text{ eV}$$

as the ground state energy. Hence, the binding energy is 2530 eV.

(c) What is the wavelength of the first line in the Lyman series for such an atom?

► From (4-22), with $Z = 1$, we have

$$\kappa = R_M \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

For the first Lyman line, $n_i = 2$ and $n_f = 1$. In this case, $R_M = (\mu/m_e)R_\infty = 186R_\infty$. Hence

$$\kappa = \frac{1}{\lambda} = 186R_\infty \left(1 - \frac{1}{4} \right) = 139.5R_\infty$$

With $R_\infty = 109737 \text{ cm}^{-1}$ we obtain

$$\lambda \approx 6.5 \text{ \AA}$$

so that the Lyman lines lie in the x-ray part of the spectrum. X-ray techniques are necessary, therefore, to study the spectrum of muonic atoms.

Example 4-10. Ordinary hydrogen contains about one part in 6000 of *deuterium*, or heavy hydrogen. This is a hydrogen atom whose nucleus contains a proton and a neutron. How does the doubled nuclear mass affect the atomic spectrum?

► The spectrum would be identical if it were not for the correction for finite nuclear mass. For a normal hydrogen atom

$$R_H = R_\infty \frac{\mu}{m} = \frac{R_\infty}{\left(1 + \frac{m}{M}\right)} = \frac{109737 \text{ cm}^{-1}}{\left(1 + \frac{1}{1836}\right)} = 109678 \text{ cm}^{-1}$$

For an atom of heavy hydrogen, or deuterium

$$R_D = R_\infty \frac{\mu}{m} = \frac{R_\infty}{\left(1 + \frac{m}{M}\right)} = \frac{109737 \text{ cm}^{-1}}{\left(1 + \frac{1}{2 \times 1836}\right)} = 109707 \text{ cm}^{-1}$$

Hence, R_D is a bit larger than R_H , so that the spectral lines of the deuterium atom are shifted to slightly shorter wavelengths compared to hydrogen.

Indeed, deuterium was discovered in 1932 by H. C. Urey following the observation of these shifted spectral lines. By increasing the concentration of the heavy isotope above its normal value in a hydrogen discharge tube, we now can enhance the intensity of the deuterium lines which, ordinarily, are difficult to detect. We then readily observe pairs of hydrogen lines; the shorter wavelength members of the pair correspond exactly to those predicted from R_D earlier. The resolution needed is easily obtained, the H_α -line pair being separated by about 1.8 Å, for example, several thousand times greater than the minimum resolvable separation.

4-8 ATOMIC ENERGY STATES

The Bohr model predicts that the total energy of an atomic electron is quantized. For example, (4-18) gives the allowed energy values for the electron in a one-electron atom. Although we have not attempted to derive similar expressions for the electrons in a multielectron atom, it is clear that according to the model the total energy of each of the electrons will also be quantized and, consequently, that the same must be true of the atom's total energy content. The Planck theory of blackbody radiation had also predicted that in the process of emission and absorption of radiation, the atoms in the cavity wall behaved as though they had quantized energy states. Hence, according to the old quantum theory every atom can have only certain discretely separated energy states.

Direct confirmation that the internal energy states of an atom are quantized came from a simple experiment performed by Franck and Hertz in 1914. The type of apparatus used by these investigators is indicated in Figure 4-13. Electrons are emitted thermally at low energy from the heated cathode C . They are accelerated to the anode A by a potential V applied between the two electrodes. Some of the electrons pass through holes in A and travel to plate P , providing their kinetic energy upon leaving A is enough to overcome a small retarding potential V_r applied between P and A . The entire tube is filled at a low pressure with a gas or vapor of the atoms to be investigated. The experiment involves measuring the electron current

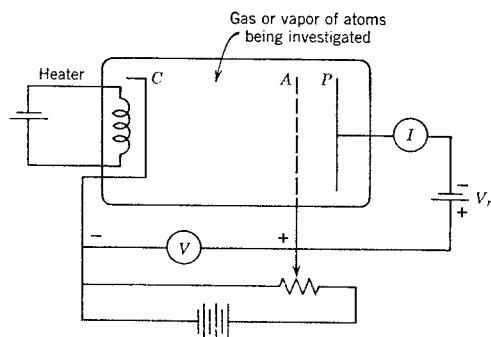


Figure 4-13 Schematic of the apparatus used by Franck and Hertz to prove that atomic energy states are quantized.

reaching P (indicated by the current I flowing through the meter) as a function of the accelerating voltage V .

The first experiment was performed with the tube containing Hg vapor. The nature of the results are indicated in Figure 4-14. At low accelerating voltage, the current I is observed to increase with increasing voltage V . When V reaches 4.9 V, the current abruptly drops. This was interpreted as indicating that some interaction between the electrons and the Hg atoms suddenly begins when the electrons attain a kinetic energy of 4.9 eV. Apparently a significant fraction of the electrons of this energy excite the Hg atoms and in so doing entirely lose their kinetic energy. If V is only slightly more than 4.9 V, the excitation process must occur just in front of the anode A , and after the process the electrons cannot gain enough kinetic energy in falling toward A to overcome the retarding potential V_r , and reach plate P . At somewhat larger V , the electrons can gain enough kinetic energy after the excitation process to overcome V_r , and reach P . The sharpness of the break in the curve indicates that electrons of energy less than 4.9 eV are not able to transfer their energy to an Hg atom. This interpretation is consistent with the existence of discrete energy states for the Hg atom. Assuming the first excited state of Hg to be 4.9 eV higher in energy than the ground state, an Hg atom would simply not be able to accept energy from the bombarding electrons unless these electrons had at least 4.9 eV.

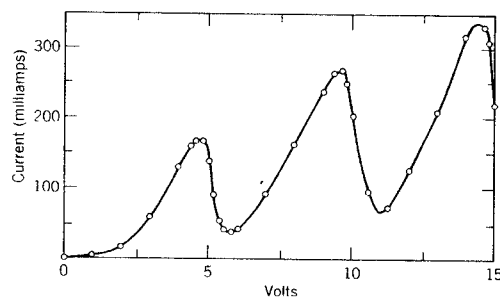


Figure 4-14 The voltage dependence of the current measured in the Franck-Hertz experiment.

Now, if the separation between the ground state and the first excited state is actually 4.9 eV, there should be a line in the Hg emission spectrum corresponding to the atom's loss of 4.9 eV in undergoing a transition from the first excited state to the ground state. Franck and Hertz found that when the energy of the bombarding electrons is less than 4.9 eV no spectral lines at all are emitted from the Hg vapor in the tube, and when the energy is not more than a few electron volts greater than this value only a single line is seen in the spectrum. This line is of wavelength 2536 Å, which corresponds exactly to a photon energy of 4.9 eV.

The Franck-Hertz experiment provided striking evidence for the quantization of the energy of atoms. It also provided a method for the direct measurement of the energy differences between the quantum states of an atom—the answers appear on the dial of a voltmeter! When the curve of I versus V is extended to higher voltages, additional breaks are found. Some are due to electrons exciting the first excited state of the atoms on several separate occasions in their trip from C to A ; but some are due to excitation of the higher excited states and, from the position of these breaks, the energy differences between the higher excited states and the ground state can be directly measured.

Another experimental method of determining the separations between the energy states of an atom is to measure its atomic spectrum and then empirically to construct a set of energy states which would lead to such a spectrum. In practice this is often quite difficult to do since the set of lines constituting the spectrum, as well as the set of energy states, is often very complicated; however, in common with all spectroscopic techniques, it is a very accurate method. In all cases in which determinations of the separations between the energy states of a certain atom have been made, using both this technique and the Franck-Hertz technique, the results have been found to be in excellent agreement.

In order to illustrate the preceding discussion, we show in Figure 4-15 a considerably simplified representation of the energy states of Hg in terms of an energy-level diagram. The separations between the ground state and the first and second excited states are known, from the Franck-Hertz experiment, to be 4.9 eV and 6.7 eV. These numbers can be confirmed, and in fact determined with much higher accuracy, by measuring the wavelengths of the two spectral lines corresponding to transitions of an electron in the Hg atom from these two states to the ground state. The energy $\mathcal{E} = -10.4$ eV, of the ground state relative to a state of zero total energy, is not determined by the Franck-Hertz experiment. However, it can be found by measuring the wavelength of the line corresponding to a transition of an atomic electron from

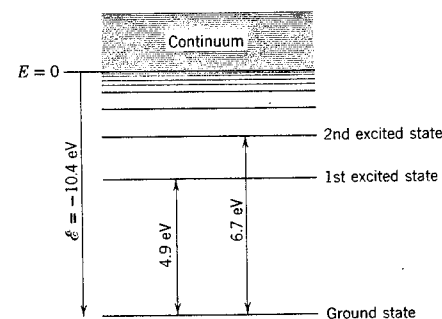


Figure 4-15 A considerably simplified energy-level diagram for mercury. Lying above the highest discrete energy level at $E = 0$ is a continuum of levels.

a state of zero total energy to the ground state. This is the series limit of the series terminating on the ground state. The energy ϵ can also be measured by measuring the energy which must be supplied to an Hg atom in order to send one of its electrons from the ground state to a state of zero total energy. Since an electron of zero total energy is no longer bound to the atom, ϵ is the energy required to ionize the atom and is therefore called the *ionization energy*.

Lying above the highest discrete state at $E = 0$ are the energy states of the system consisting of an unbound electron plus an ionized Hg atom. *The total energy of an unbound electron (a free electron with $E > 0$) is not quantized.* Thus any energy $E > 0$ is possible for the electron, and the energy states form a continuum. The electron can be excited from its ground state to a continuum state if the Hg atom receives an energy greater than 10.4 eV. Conversely, it is possible for an ionized Hg atom to capture a free electron into one of the quantized energy states of the neutral atom. In this process, radiation of frequency greater than the series limit corresponding to that state will be emitted. The exact value of the frequency depends on the initial energy E of the free electron. Since E can have any value, the spectrum of Hg should have a continuum extending beyond every series limit in the direction of increasing frequency. This can actually be seen experimentally, although with some difficulty. These comments concerning the continuum of energy states for $E > 0$, and its consequences, have been made in reference to the Hg atom, but they are equally true for all atoms.

4-9 INTERPRETATION OF THE QUANTIZATION RULES

The success of the Bohr model, as measured by its agreement with experiment, was certainly very striking; but it only accentuated the mysterious nature of the postulates on which the model was based. One of the biggest mysteries was the question of the relation between Bohr's quantization of the angular momentum of an electron moving in a circular orbit and Planck's quantization of the total energy of an entity, such as an electron, executing simple harmonic motion. In 1916 some light was shed upon this by Wilson and Sommerfeld, who enunciated a set of rules for the quantization of any physical system for which the coordinates are periodic functions of time. These rules included both the Planck and the Bohr quantization as special cases. They were also of considerable use in broadening the range of applicability of the quantum theory. These rules can be stated as follows:

For any physical system in which the coordinates are periodic functions of time, there exists a quantum condition for each coordinate. These quantum conditions are

$$\oint p_q dq = n_q h \quad (4-23)$$

where q is one of the coordinates, p_q is the momentum associated with that coordinate, n_q is a quantum number which takes on integral values, and \oint means that the integration is taken over one period of the coordinate q .

The meaning of these rules can best be illustrated in terms of some specific examples. Consider a one-dimensional simple harmonic oscillator. Its total energy can be written, in terms of position and momentum, as

$$E = K + V = \frac{p_x^2}{2m} + \frac{kx^2}{2}$$

or

$$\frac{p_x^2}{2mE} + \frac{x^2}{2E/k} = 1$$

The quantization integral $\oint p_x dx$ is most easily evaluated, for the relation between p_x and x that is imposed by this equation, if we consider a geometric interpretation. The relation between p_x and x is the equation of an ellipse. Any instantaneous state of motion of the oscillator is represented by some point in a plot of this equation on a two-dimensional space having coordinates p_x and x . We call such a space (the p - q plane) *phase space*, and the plot is a *phase diagram* of the linear oscillator, shown in Figure 4-16. During one cycle of oscillation the point representing the position and momentum of the particle travels once around the ellipse. The semiaxes a and b of the ellipse $p_x^2/h^2 + x^2/a^2 = 1$ are seen, by comparison with our equation, to be

$$b = \sqrt{2mE} \quad \text{and} \quad a = \sqrt{2E/k}$$

Now the area of an ellipse is πab . Furthermore, the value of the integral $\oint p_x dx$ is just equal to that area. (To see this note that the integral over a complete oscillation equals an integral in which the representative point travels from $x = -a$ to $x = +a$ over the upper half of the ellipse plus an integral in which the point travels back to $x = -a$ over the lower half. In the first integral both p_x and dx are positive and its value equals the area enclosed between the upper half and the x axis; in the second both p_x and dx are negative so the value of the integral is positive and equals the area enclosed between the lower half of the ellipse and the x axis.) Thus we obtain

$$\oint p_x dx = \pi ab$$

In our case

$$\oint p_x dx = \frac{2\pi E}{\sqrt{k/m}}$$

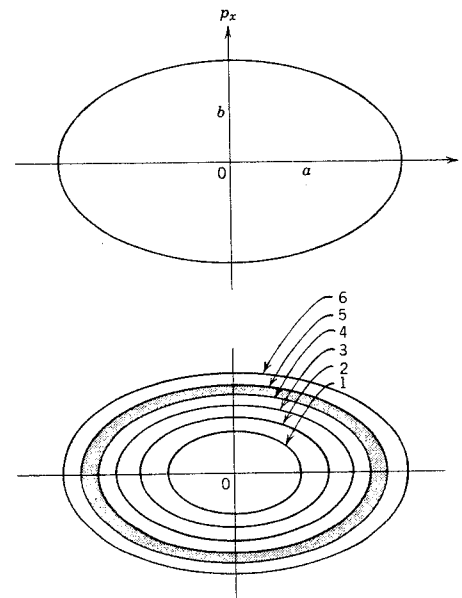


Figure 4-16 Top: A phase space diagram of the motion of the representative point for a linear simple harmonic oscillator. Bottom: The allowed energy states of the oscillator are represented by ellipses whose areas in phase space are given by nh . The space between adjacent ellipses (for example the shaded area) has an area h .

but

$$\sqrt{k/m} = 2\pi\nu$$

where ν is the frequency of the oscillation, so that

$$\oint p_x dx = E/\nu$$

If we now use (4-23), the Wilson-Sommerfeld quantization rule, we have

$$\oint p_x dx = E/\nu = n_x h \equiv nh$$

or

$$E = nh\nu$$

which is identical with Planck's quantization law.

Note that the allowed states of oscillation are represented by a series of ellipses in phase space, the area enclosed between successive ellipses always being h (see Figure 4-16). Again we find that the classical situation corresponds to $h \rightarrow 0$, all values of E and hence all ellipses being allowed if that were true. The quantity $\oint p_x dx$ is sometimes called a *phase integral*; in classical physics it is the integral of the dynamical quantity called the *action* over one oscillation of the motion. Hence, the Planck energy quantization is equivalent to the *quantization of action*.

We can also deduce the Bohr quantization of angular momentum from the Wilson-Sommerfeld rule, (4-23). An electron moving in a circular orbit of radius r has an angular momentum, $mvr = L$, which is constant. The angular coordinate is θ , which is a periodic function of the time. That is, θ versus t is a saw-tooth function, increasing linearly from zero to 2π rad in one period and repeating this pattern in each succeeding period. The quantization rule

$$\oint p_\theta d\theta = n_\theta h$$

becomes, in this case

$$\oint L d\theta = nh$$

and

$$\oint L d\theta = L \int_0^{2\pi} d\theta = 2\pi L$$

so that

$$2\pi L = nh$$

or

$$L = nh/2\pi \equiv nh$$

which is identical with Bohr's quantization law.

A more physical interpretation of the Bohr quantization rule was given in 1924 by de Broglie. The Bohr quantization of angular momentum can be written as in (4-15) as

$$mvr = pr = nh/2\pi \quad n = 1, 2, 3, \dots$$

where p is the linear momentum of an electron in an allowed orbit of radius r . If we substitute into this equation the expression for p in terms of the corresponding de

Broglie wavelength

$$p = h/\lambda$$

the Bohr equation becomes

$$hr/\lambda = nh/2\pi$$

or

$$2\pi r = n\lambda \quad n = 1, 2, 3, \dots \quad (4-24)$$

Thus the allowed orbits are those in which the circumference of the orbit can contain exactly an integral number of de Broglie wavelengths.

Imagine the electron to be moving in a circular orbit at constant speed, with the associated wave following the electron. The wave, of wavelength λ , is then wrapped repeatedly around the circular orbit. The resultant wave that is produced will have zero intensity at any point unless the wave at each traversal is exactly in phase at that point with the wave in other traversals. If the waves in each traversal are exactly in phase, they join on perfectly in orbits that accommodate integral numbers of de Broglie wavelengths, as illustrated in Figure 4-17. But the condition that this happens is just the condition that (4-24) be satisfied. If this equation were violated, then in a large number of traversals the waves would interfere with each other in such a way that their average intensity would be zero. Since the average intensity of the waves, Ψ^2 , is supposed to be a measure of where the particle is located, we interpret this as meaning that an electron cannot be found in such an orbit.

This wave picture gives no suggestion of progressive motion. Rather, it suggests standing waves, as in a stretched string of a given length. In a stretched string only certain wavelengths, or frequencies of vibration, are permitted. Once such modes are excited, the vibration goes on indefinitely if there is no damping. To get standing waves, however, we need oppositely directed traveling waves of equal amplitude. For the atom this requirement is presumably satisfied by the fact that the electron can traverse an orbit in either direction and still have the magnitude of angular momentum required by Bohr. The de Broglie standing wave interpretation, illustrated in Figure 4-17, therefore provides a satisfying basis for Bohr's quantization rule and, for this case, of the more general Wilson-Sommerfeld rule.

There is another example of a system in which the origin of the Wilson-Sommerfeld quantization rule can be understood in terms of the requirement that the de Broglie

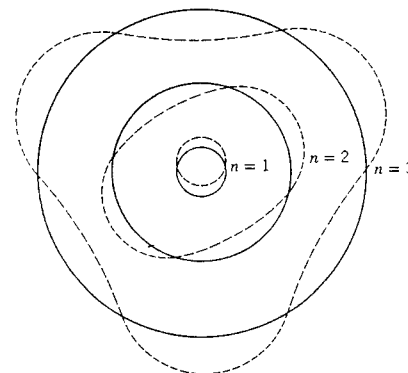


Figure 4-17 Illustrating standing de Broglie waves set up in the first three Bohr orbits. The locations of the nodes can, of course, be found anywhere on each orbit provided that their spacings are as shown.

waves associated with a particle undergoing periodic motion form a set of standing waves. Consider a particle which moves freely along the x axis from $x = -a/2$ to $x = +a/2$, but which does not penetrate into the regions outside these limits. This system can be thought of as representing approximately the motion of a conduction electron in a one-dimensional piece of metal that extends from $-a/2$ to $+a/2$. The particle bounces back and forth between the ends of the region with momentum p_x that changes sign at each bounce, but maintains a constant magnitude p . So the Wilson-Sommerfeld equation reads

$$\oint p_x dx = p \oint dx = p2a = nh$$

or

$$n \frac{h}{p} = 2a \quad (4-25)$$

But h/p is just the de Broglie wavelength λ of the particle, so we have

$$n\lambda = 2a$$

Thus an integral number of de Broglie wavelengths just fits into the distance covered by the particle in one traversal of the region, and this allows the waves associated with successive traversals to be in phase and so set up a standing wave.

We shall see in the following chapters that the properties of standing waves are equally important in the quantization conditions of Schroedinger's quantum mechanics. And the time-independent features of the standing wave associated with an electron in the ground state of an atom will make it possible to understand in a simple way the fundamental question of why the electron does not emit electromagnetic radiation and spiral into the nucleus.

4-10 SOMMERFELD'S MODEL

One of the important applications of the Wilson-Sommerfeld quantization rules is to the case of a hydrogen atom in which it was assumed that the electron could move in elliptical orbits. This was done by Sommerfeld in an attempt to explain the *fine structure* of the hydrogen spectrum. The fine structure is a splitting of the spectral lines, into several distinct components, which is found in all atomic spectra. It can be observed only by using equipment of very high resolution since the separation, in terms of reciprocal wavelength, between adjacent components of a single spectral line is of the order of 10^{-4} times the separation between adjacent lines. According to the Bohr model, this must mean that what we had thought was a single energy state of the hydrogen atom actually consists of several states which are very close together in energy.

Sommerfeld first evaluated the size and shape of the allowed elliptical orbits, as well as the total energy of an electron moving in such an orbit, using the formulas of classical mechanics. Describing the motion in terms of the polar coordinates r and θ , he applied the two quantum conditions

$$\oint L d\theta = n_\theta h$$

$$\oint p_r dr = n_r h$$

The first condition yields the same restriction on the orbital angular momentum

$$L = n_\theta h \quad n_\theta = 1, 2, 3, \dots$$

that it does for the circular orbit theory. The second condition (which was not applicable in the limiting case of purely circular orbits) leads to the following relation

between L and a/b , the ratio of the semimajor axis to the semiminor axis of the ellipse

$$L(a/b - 1) = n_r h \quad n_r = 0, 1, 2, 3, \dots$$

By applying the condition of mechanical stability analogous to (4-14), a third equation is obtained. From these equations Sommerfeld evaluated the semimajor and semiminor axes a and b , which give the size and shape of the elliptical orbits, and also the total energy E of an electron in such an orbit. The results are

$$a = \frac{4\pi\epsilon_0 n^2 h^2}{\mu Z e^2} \quad (4-26a)$$

$$b = a \frac{n_\theta}{n} \quad (4-26b)$$

$$E = -\left(\frac{1}{4\pi\epsilon_0}\right)^2 \frac{\mu Z^2 e^4}{2n^2 h^2} \quad (4-26c)$$

where μ is the reduced mass of the electron, and where the quantum number n is defined by

$$n \equiv n_\theta + n_r$$

Since $n_\theta = 1, 2, 3, \dots$ and $n_r = 0, 1, 2, 3, \dots$, n can take on the values

$$n = 1, 2, 3, 4, \dots$$

For a given value of n , n_θ can assume only the values

$$n_\theta = 1, 2, 3, \dots, n$$

The integer n is called the *principal quantum number*, and n_θ is called the *azimuthal quantum number*.

Equation (4-26b) shows that the shape of the orbit (the ratio of the semimajor to the semiminor axes) is determined by the ratio of n_θ to n . For $n_\theta = n$ the orbits are circles of radius a . Note that the equation giving a in terms of n is identical with (4-16), the equation giving the radius of the circular Bohr orbits. (Remember that (4-16) will have m replaced by μ if proper account is taken of the finite nuclear mass.) Figure 4-18 shows, to scale, the possible orbits corresponding to the first three values of the principal quantum number. Corresponding to each value of the principal quantum number n there are n different allowed orbits. One of these, the circular orbit, is just the orbit described by the original Bohr model. The others are elliptical. But despite the very different paths followed by an electron moving in the different possible orbits for a given n , (4-26c) tells us that the total energy of the electron is the same. The total energy of the electron depends only on n . The several orbits characterized by a common value of n are said to be *degenerate*. The energies of different states of motion "degenerate" to the same total energy.

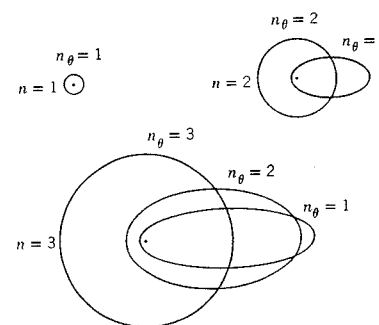


Figure 4-18 Some elliptical Bohr-Sommerfeld orbits. The nucleus is located at the common focus of the ellipses, indicated by the dot.

This degeneracy in the total energy of an electron, following the orbits of very different shape but common n , is the result of a very delicate balance between potential and kinetic energy, which is characteristic of treating the inverse square Coulomb force by the methods of classical mechanics. Exactly the same phenomenon is found in planetary or satellite motion, which is governed by the inverse square gravitational force. For instance, a satellite may be launched into any one of a whole family of elliptical orbits, all of which correspond to the same total energy and have the same semimajor axis. Of course there is effectively no quantization of the orbit parameters in these macroscopic cases, but as far as degeneracy is concerned they are completely analogous to the case of a hydrogen atom.

Sommerfeld "removed the degeneracy" in the hydrogen atom by next treating the problem *relativistically*. In the discussion following (4-17) we showed that, for an electron in a hydrogen atom, $v/c \approx 10^{-2}$ or less. Thus we would expect the relativistic corrections to the total energy, due to the relativistic variation of the electron mass which will be of the order of $(v/c)^2$, to be only of the order of 10^{-4} ; however, this is just the order of magnitude of the splitting in the energy states of hydrogen that would be needed to explain the fine structure of the hydrogen spectrum. The actual size of the correction depends on the average velocity of the electron which, in turn, depends on the ellipticity of the orbit. After a calculation which is much too tedious to reproduce here, Sommerfeld showed that the total energy of an electron in an orbit characterized by the quantum numbers n and n_θ is equal to

$$E = -\frac{\mu Z^2 e^4}{(4\pi\epsilon_0)^2 2n^2 \hbar^2} \left[1 + \frac{\alpha^2 Z^2}{n} \left(\frac{1}{n_\theta} - \frac{3}{4n} \right) \right] \quad (4-27a)$$

The quantity α is a pure number called the *fine structure constant*. Its value is

$$\alpha \equiv \frac{1}{4\pi\epsilon_0} \frac{e^2}{\hbar c} = 7.297 \times 10^{-3} \approx \frac{1}{137} \quad (4-27b)$$

In Figure 4-19 we represent the first few energy states of the hydrogen atom in terms of an energy-level diagram. The separation between the several levels with a common value of n has been greatly exaggerated for the sake of clarity. Arrows indicate transitions between the various energy states which produce the lines of the atomic spectrum. Lines corresponding to the transitions represented by the solid arrows are observed in the hydrogen spectrum. The wavelengths of these lines are in very good agreement with the predictions derived from (4-27a).

However, the lines corresponding to the transitions represented by dashed arrows in Figure 4-19 are not found in the spectrum. The transitions concerned do not take place. Inspection of the figure will demonstrate that transitions only occur if

$$n_{\theta i} - n_{\theta f} = \pm 1 \quad (4-28)$$

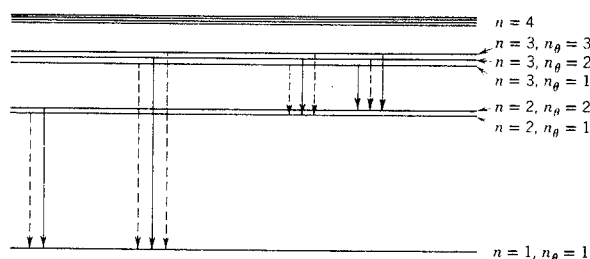


Figure 4-19 The fine-structure splitting of some energy levels of the hydrogen atom. The splitting is greatly exaggerated. Transitions which produce observed lines of the hydrogen spectrum are indicated by solid arrows.

This is called a *selection rule*. It selects from all the transitions those that actually occur.

4-11 THE CORRESPONDENCE PRINCIPLE

A justification of selection rules could sometimes be found with the aid of an auxiliary postulate known as the *correspondence principle*. This principle, enunciated by Bohr in 1923, consists of two parts:

1. *The predictions of the quantum theory for the behavior of any physical system must correspond to the prediction of classical physics in the limit in which the quantum numbers specifying the state of the system become very large.*

2. *A selection rule holds true over the entire range of the quantum number concerned. Thus any selection rules which are necessary to obtain the required correspondence in the classical limit (large n) also apply in the quantum limit (small n).*

Concerning the first part, it is obvious that the quantum theory must correspond to the classical theory in the limit in which the system behaves classically. The only question is: Where is the classical limit? Bohr's assumption is that the classical limit is always to be found in the limit of large quantum numbers. In making this assumption he was guided by certain evidence available at the time. For instance, the classical Rayleigh-Jeans theory of the blackbody spectrum agrees with experiment in the limit of small ν . Since Planck's quantum theory agrees with experiment everywhere, we see that correspondence between the quantum and classical theories is found, in this case, in the limit of small ν . But it is easy to see that as ν becomes small the average value \bar{n} , of the quantum number specifying the energy state of blackbody electromagnetic waves of frequency ν , will become large. (Since $E = nh\nu$, we have $\bar{E} = \bar{n}h\nu$. But as $\nu \rightarrow 0$, $\bar{E} \rightarrow kT$, so in this limit $\bar{n}h\nu = kT$, which is a constant. Thus $\bar{n} \rightarrow \infty$ as $\nu \rightarrow 0$ in the classical limit. Note also that if we fix ν in the relation $\bar{n}h\nu = kT = \text{const.}$ and take $h \rightarrow 0$ as we frequently have in considering the classical limit, we again find $\bar{n} \rightarrow \infty$ in that limit.) The second part of the correspondence principle was purely an assumption, but certainly a reasonable one.

Let us illustrate the correspondence principle by applying it to a simple harmonic oscillator, such as a pendulum oscillating at frequency ν . One prediction of quantum theory for this system is that the allowed energy states are given by $E = nh\nu$. In the discussion in Chapter 1, we saw that, in the limit of large n , this prediction is not in disagreement with what we actually know about the energy states of a classical pendulum. In this case of a simple harmonic oscillator, the quantum and classical theories do correspond for $n \rightarrow \infty$ insofar as the energy states are concerned. Next assume that the pendulum bob carries an electric charge, so that we can compare the predictions of the two theories concerning the emission and absorption of electromagnetic radiation by such a system. Classically the system would emit radiation due to the accelerated motion of the charge, and the frequency of the emitted radiation would be exactly ν . According to the quantum physics, radiation is emitted as a result of the system making a transition from quantum state n_i to quantum state n_f . The energy emitted in such a transition is equal to $E_i - E_f = (n_i - n_f)h\nu$. This energy is carried away by a photon of frequency $(E_i - E_f)/h = (n_i - n_f)\nu$. Thus, in order to obtain correspondence between the classical and quantum predictions of the frequency of the emitted radiation, we must require that the selection rule $n_i - n_f = 1$ be valid in the classical limit of large n . A similar argument concerning the absorption of radiation by the charged pendulum shows that in the classical limit there is also the possibility of a transition in which $n_i - n_f = -1$. The validity of these selection rules in the quantum limit of small n can be tested by investigating the spectrum of radiation emitted by a vibrating diatomic molecule. The vibrational energy states for such a system are just those of a simple harmonic oscillator, since the force which

Table 4-2 The Correspondence Principle for Hydrogen

n	v_0	ν	% Difference
5	5.26×10^{13}	7.38×10^{13}	29
10	6.57×10^{12}	7.72×10^{12}	14
100	6.578×10^9	6.677×10^9	1.5
1,000	6.5779×10^6	6.5878×10^6	0.15
10,000	6.5779×10^3	6.5789×10^3	0.015

leads to the equilibrium separation of the two atoms has the same form as a harmonic restoring force. From the vibrational spectrum it can be determined that the selection rule $n_i - n_f = \pm 1$ actually is in operation in the limit of small quantum numbers, in agreement with the second part of the correspondence principle.

A number of other selection rules were discovered empirically in the analysis of atomic and molecular spectra. Sometimes, but not always, it was possible to understand these selection rules in terms of a correspondence principle argument.

Example 4-11. Apply the correspondence principle to hydrogen atom radiation in the classical limit.

► The frequency of revolution v_0 of an electron in a Bohr orbit follows from (4-16) and (4-17) and is given by

$$v_0 = \frac{v}{2\pi r} = \left(\frac{1}{4\pi\epsilon_0} \right)^2 \frac{me^4}{4\pi\hbar^3} \frac{2}{n^3}$$

According to classical physics the frequency of the light emitted in such a case is equal to v_0 , the frequency of revolution.

Quantum physics predicts that the frequency ν of the emitted light is, from (4-19)

$$\nu = \frac{c}{\lambda} = cR = \left(\frac{1}{4\pi\epsilon_0} \right)^2 \frac{me^4}{4\pi\hbar^3} \left[\frac{1}{n_f^2} - \frac{1}{n_i^2} \right]$$

But, if this is to agree with v_0 , we must have $n_i - n_f = 1$ as a selection rule for large quantum numbers. To see this, take $n_i - n_f = 1$ and obtain

$$\nu = \left(\frac{1}{4\pi\epsilon_0} \right)^2 \frac{me^4}{4\pi\hbar^3} \left[\frac{1}{(n-1)^2} - \frac{1}{n^2} \right] = \left(\frac{1}{4\pi\epsilon_0} \right)^2 \frac{me^4}{4\pi\hbar^3} \left[\frac{2n-1}{(n-1)^2 n^2} \right]$$

where $n_i = n$ and $n_f = n - 1$. Then as $n \rightarrow \infty$ the expression in the square brackets above approaches $2/n^3$ so that $\nu \rightarrow v_0$ as $n \rightarrow \infty$.

In Table 4-2 we illustrate the correspondence for large n .

It is instructive to note that although both parts of the correspondence principle lead to agreement with experiment for the simple harmonic oscillator, only the first part agrees with experiment in the hydrogen atom considered in the preceding example. For experiment shows that the selection rule $n_i - n_f = 1$, which was necessary to satisfy the first part of the principle for large n , does *not* apply to the hydrogen atom for small n . Transitions are observed to occur between states of low n , in which the quantum numbers differ in value by more than one. This illustrates the fact that the old quantum theory cannot always be made to agree with experiment, however it is patched up.

4-12 A CRITIQUE OF THE OLD QUANTUM THEORY

In the past four chapters we have discussed some of the developments which led to modern quantum mechanics. These developments are now referred to as the *old quantum theory*. In many respects this theory was very successful, even more so than may be apparent to the student because we have not mentioned a number of success-

ful applications of the old quantum theory to phenomena, such as the heat capacity of solids at low temperature, which were inexplicable in terms of the classical theories. However, the old quantum theory certainly was not free of criticism. To complete our discussion of this theory we must indicate some of its undesirable aspects:

1. The theory only tells us how to treat systems which are periodic, by using the Wilson-Sommerfeld quantization rules, but there are many systems of physical interest which are not periodic. And the number of periodic systems for which a physical basis of these rules can be found in the de Broglie relation is very small.

2. Although the theory does tell us how to calculate the energies of the allowed states of certain systems, and the frequency of the photons emitted or absorbed when a system makes a transition between allowed states, it does not tell us how to calculate the *rate* at which such transitions take place. For example, it does not tell us how to calculate the intensities of spectral lines. And we have seen that the theory cannot always tell us even which transitions actually are observed to occur and which are not.

3. When applied to atoms, the theory is really only successful for one-electron atoms. The alkali elements (Li, Na, K, Rb, Cs) can be treated approximately, but only because they are in many respects similar to a one-electron atom. The theory fails badly even when applied to the neutral He atom, which contains only two electrons.

4. Finally we might mention the subjective criticism that the entire theory seems somehow to lack coherence—to be intellectually unsatisfying.

That some of these objections are really of a very fundamental nature was realized by everyone concerned, and much effort was expended in attempts to develop a quantum theory which would be free of these and other objections. The effort was well rewarded. In 1925 Erwin Schrodinger developed his theory of *quantum mechanics*. Although it is a generalization of the de Broglie postulate, the Schrodinger theory is in some respects very different from the old quantum theory. For instance, the picture of atomic structure provided by quantum mechanics is the antithesis of the picture, used in the old quantum theory, of electrons moving in well-defined orbits. Nevertheless, the old quantum theory is still frequently employed as a first approximation to the more accurate description of quantum phenomena provided by quantum mechanics. The reasons are that the old quantum theory is often capable of giving numerically correct results with mathematical procedures which are considerably less complicated than those used in quantum mechanics, and that the old quantum theory is often helpful in visualizing processes which are difficult to visualize in terms of the rather abstract language of quantum mechanics.

QUESTIONS

1. In a collision between an α particle and an electron, what general considerations limit the momentum transfer? Does the fact that the force is Coulombic play any role in this respect?
2. How does the Thomson atom differ from a random distribution of protons and electrons in a spherical region?
3. List objections to the Thomson model of the atom.
4. Why do we specify that the foil be thin in experiments intended to check the Rutherford scattering formula?
5. The scattering of α particles at very small angles disagrees with the Rutherford formula for such angles. Explain.
6. How does the deduction of (4-3), which gives the trajectory of a particle moving under the influence of a repulsive inverse square Coulomb force, differ from the deduction of

PART 2

STATISTICAL PHYSICS

10 Classical Statistical Mechanics

11 Thermodynamics

12 Thermal Properties of Gases

13 Quantum Statistics

In the preceding chapters of this text we have studied the fundamental constituents of matter: particles, nuclei, atoms, and molecules. But we cannot see or feel individual atoms or molecules at work. Rather we observe the result of a large number of them acting in a more or less organized manner; i.e., macroscopic processes. The properties of matter in bulk (called macroscopic properties), as we ordinarily observe them, are the result of these collective actions. The collective behavior of large numbers of atoms and molecules is basically a result of their electromagnetic interaction, since gravitational interaction plays only a minor role and the strong and weak interactions affect only nuclear processes. Familiar processes, such as melting and vaporization, diffusion, thermal and electrical conduction, emission of electrons by hot metals, and many others, as well as such concepts as temperature, heat capacity, heat of change of phase, etc., fall in this category of collective properties. It is the understanding and control of these collective phenomena that primarily interest the applied physicist, the engineer, the chemist, and other scientists in their endeavor to use the forces of nature for the welfare of man.

To describe processes involving a very large number of particles, special methods must be devised. These methods are, by necessity, of a statistical nature, since we cannot take the detailed motion of individual particles into account (nor is it necessary to make such an effort to obtain results of practical value). For this reason the discussion of macroscopic processes from the molecular point of view constitutes what is called *statistical physics*. The word "statistical" must be interpreted as applying to a technique for describing processes involving large numbers of particles whose individual interactions are known, without considering the individual behavior of each particle. In this respect, statistical methods have been applied to the discussion of many-electron atoms and many-nucleon nuclei.

In this part of the text we shall first develop the statistical method known as *classical statistical mechanics*, discuss its general applications to what is called *thermodynamics*, and apply the method to analyze the properties of gases. We shall conclude this part with a brief introduction to *quantum statistical mechanics*, illustrating some of its applications.

10 CLASSICAL STATISTICAL MECHANICS

10.1 Introduction

10.2 Statistical Equilibrium

10.3 The Maxwell-Boltzmann Distribution Law

10.4 Temperature

10.5 Thermal Equilibrium

10.6 Application to the Ideal Gas

10.1 Introduction

Mechanics is founded on certain general principles, such as the conservation of energy and momentum, that are applicable to the motion of interacting particles. In this chapter we shall extend the principles of mechanics to systems of many particles, emphasizing the methods used to obtain collective or macroscopic properties of the system, without considering the detailed motion of each particle. This technique is called *statistical mechanics*. We use "particle" here in a broad sense, meaning a fundamental particle, such as an electron, or an aggregate of fundamental particles, such as an atom or molecule. Thus a "particle" will be each of the well-defined and stable units composing a given physical system.

The fact that we need a statistical approach when we are dealing with the macroscopic properties of matter is easily recognized when we note that in one cubic centimeter of a gas at STP there are about 3×10^{19} molecules. It is not only practically impossible, but also unnecessary to take into account the motions of each of these molecules in detail to determine the bulk properties of the gas, such as its pressure or temperature. On the other hand, to make a statistical analysis of a many-particle system, we have to make some reasonable estimate about the dynamical state of each particle based on the general properties of the particles. We make this estimate by introducing the concept of the *probability of distribution* of the particles among the different dynamical states in which they may be found. When we introduce the idea of probability, this does not imply that we assume that the particles move randomly or in a chaotic way, without obeying any well-defined laws. The concept of probability arises from our method of estimating the dynamical states of the particles in a system, not from the mechanism by which, as a result of their interactions, the particles of a system are distributed in nature among the possible dynamical states. Hence the validity of the statistical analysis of a many-particle system is directly related to the validity of our assumptions concerning the probability distribution of the particles.

10.2 Statistical Equilibrium

Consider an isolated system composed of a large number N of particles, in which each particle has available to it several states with energies E_1, E_2, E_3, \dots . The energy states may be quantized (as are the rotational and vibrational states in a molecule) or they may form a practically continuous spectrum (as for the translational kinetic energy of the molecules in a gas). At a particular time the particles are distributed among the different states, so that n_1 particles have energy E_1 ; n_2 particles have energy E_2 ; and so on. The total number of particles is

$$N = n_1 + n_2 + n_3 + \dots = \sum_i n_i \quad (10.1)$$

and we assume that it remains constant for all processes occurring in the system. The total energy of the system is

$$U = n_1 E_1 + n_2 E_2 + n_3 E_3 + \dots = \sum_i n_i E_i \quad (10.2)$$

This expression for the total energy of the system implicitly assumes that the particles are noninteracting (or that they interact only slightly), so that to each particle we can attribute an energy depending only on the coordinates of the particle. If we consider interactions, we must add to Eq. (10.2) terms of the form $E_{p12} + E_{p13} + \dots + E_{p23} + \dots$ corresponding to the potential energy of interaction between pairs of particles. Each term includes the coordinates of both interacting particles. In such a case we cannot speak of the energy of each particle, but only of the system.

It may seem at first sight that our discussion is therefore unrealistic, since all particles that make up physical systems are interacting. However, under special conditions we can use a technique called the *self-consistent field*, in which each particle is considered subject to the *average* interaction of the others, with an average potential energy which depends only on its coordinates, so that we can still write U as in Eq. (10.2), but now $E_i = E_{ki} + E_{pi \text{ ave.}}$ For cases in which the interactions among the particles must be considered explicitly, other techniques must be used. We shall discuss these in Chapter 12 in connection with real gases.

If the system is isolated, the total energy U must be constant. However, as a result of their mutual interactions and collisions, the distribution of the particles among the available energy states may be changing. For example, in a gas a fast molecule may collide with a slow one; after the collision the fast molecule may have slowed down and the slow one may have sped up. Or an excited atom may collide inelastically with another atom, with a transfer of its excitation energy into kinetic energy of both atoms. Hence, in both examples, the particles after the collision are in different states. In other words, the numbers n_1, n_2, n_3, \dots , which give the partition (or distribution) of the N particles among the available energy states, may be changing. It is reasonable to assume that for each macroscopic state of a system of particles there is a partition which is more favored than any other. In other words, we may say that, given the physical conditions of the system of particles (that is, the number of particles, the total energy, and the structure of each particle), there is a most probable partition. When this partition is achieved, the system is said to be in *statistical equilibrium*.

A system in statistical equilibrium will not depart from the most probable partition (except for statistical fluctuations) unless it is disturbed by an external action. By this we mean that the partition numbers n_1, n_2, n_3, \dots may fluctuate around the values corresponding to the most probable partition without noticeable (or observable) macroscopic effects. For example, suppose that we have a gas in statistical equilibrium, in which a molecule of energy E_i collides with a molecule of energy E_j ; after the collisions their energies are E_r and E_s . We may assume that within a short time another pair of molecules is removed from energy states E_r and E_s and the same or another pair of molecules is moved into energy states E_i and E_j , so that, statistically, the partition has not changed.

The key problem of statistical mechanics is to find the most probable partition (or distribution law) of an isolated system, given its composition. Once the most probable partition has been found, the next problem is to devise methods for de-

iving the macroscopically observed properties from it. To obtain the distribution law, certain assumptions are required. One may try several plausible assumptions, until a distribution law in accordance with experimental results is obtained. Three distribution laws or statistics are presently used. One is called the Maxwell-Boltzmann distribution law, which is the basis of classical statistics. We shall study it in this chapter.

Classical statistical mechanics was developed in the last part of the nineteenth century and the beginning of the twentieth century as the result of the work of Ludwig Boltzmann (1844–1906), James C. Maxwell (1831–1879), and Josiah W. Gibbs (1839–1903). Classical statistical mechanics has a very broad applicability, especially to the discussion of many properties of gases. The remaining two distribution laws, called Fermi-Dirac and Bose-Einstein, belong to quantum statistics and will be considered in Chapter 13. Classical statistical mechanics can be considered as a limiting value of the two quantum statistics (see Section 13.9).

10.3 The Maxwell-Boltzmann Distribution Law

Let us consider a system composed of a large number of identical and distinguishable particles. By identical particles, we mean that the particles have the same structure and composition. By distinguishable particles, we mean that we can distinguish, or tell the difference, between one particle and another identical particle. At first sight it seems that there is a contradiction between identical and distinguishable, and indeed this is the case! Later on we shall reconsider this apparent lack of logic; however, the results we shall obtain now are sufficiently simple to justify a preliminary discussion of such a system.

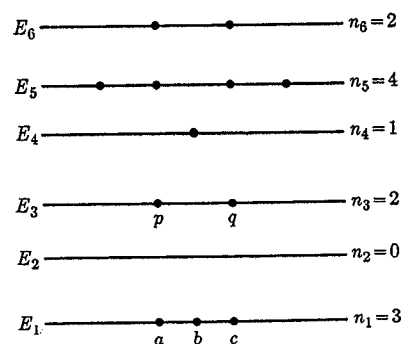


Fig. 10-1. Distribution of particles among different energy states.

Let us represent a particular partition n_1, n_2, n_3, \dots by the geometrical arrangement shown in Fig. 10-1. Each line represents a particular state of energy E_i , and the number of dots indicates the number n_i of particles in each energy state. In our example $n_1 = 3, n_2 = 0, n_3 = 2, n_4 = 1$, etc.

Our first assumption is that all energy states are equally accessible to the particles of the system; i.e., that all energy states have the same probability of being

occupied. Then we shall assume that

the probability of a particular partition is proportional to the number of different ways in which the particles can be distributed among the available energy states to produce the partition.

Let us then see, as an example, the number of different ways in which the partition of Fig. 10-1 can be obtained. By different we mean that the numbers n_1, n_2, n_3, \dots are fixed, but the particles in each state are different. That is, a partition in which particle a is in state E_1 and particle p is in state E_3 is considered different from a partition in which particle a is in state E_3 and particle p is in state E_1 . This is a consequence of assuming that the component particles are distinguishable. If they were indistinguishable, we would have to assume that the two partitions were the same.

To start filling the state E_1 , we may select the first particle from any one of the N particles available. Then there are N distinguishable ways of selecting the first particle. The second particle can be selected in $N - 1$ different ways, since only $N - 1$ particles are left available. And the third particle can be selected in $N - 2$ different ways. So the total number of different distinguishable ways in which we may select the first three particles to place in state E_1 is

$$N(N - 1)(N - 2) = \frac{N!}{(N - 3)!} \quad (10.3)$$

Let us designate the three chosen particles by a, b , and c . We may pick them in any of the $3! = 6$ different orders or permutations $abc, bca, cab, bac, acb, cba$. But these $3!$ different orders of placing particles a, b , and c in E_1 give the same partition, since they all correspond to particles a, b , and c , in state E_1 . A partition is determined only by the number and labeling of particles in each state and not by the order in which they were placed there, which is immaterial once the partition is arranged. Therefore, to obtain the total number of distinguishable different ways in which we may select the first three particles in state E_1 , we must divide Eq. (10.3) by $3!$, resulting in

$$\frac{N!}{3!(N - 3)!}$$

The general expression for the total number of distinguishable different ways of placing n_1 particles in state E_1 is then

$$\left| \frac{N!}{n_1!(N - n_1)!} \right| \quad (10.4)$$

This is just the number of permutations of N objects, taken n_1 at a time. When we pass to the second state E_2 , only $N - n_1$ particles are available. So if we want to place n_2 particles in state E_2 , we must use Eq. (10.4) with N replaced by $N - n_1$

and n_1 replaced by n_2 , resulting in

$$\left[\frac{(N - n_1)!}{n_2!(N - n_1 - n_2)!} \right] \quad (10.5)$$

For the third state we have only $N - n_1 - n_2$ particles left, and we are placing n_3 particles in it, so that instead of Eq. (10.4) we get

$$\frac{(N - n_1 - n_2)!}{n_3!(N - n_1 - n_2 - n_3)!}$$

The process can be continued until all energy states have been considered. The total number of distinguishable different ways of obtaining the partition n_1, n_2, n_3, \dots is obtained by multiplying expressions (10.4), (10.5), and the successive expressions for all remaining energy states. In doing this the student may note that a number of factors, such as $(N - n_1)!$, $(N - n_1 - n_2)!$ etc., cancel out, resulting in the simplified expression

$$P = \frac{N!}{n_1!n_2!n_3!\dots}, \quad (10.6)$$

which gives the number of different distinguishable ways in which the partition n_1, n_2, n_3, \dots can be obtained. We shall now assume that the probability of obtaining that partition is proportional to P . For example, for the partition of Fig. 10-1, the probability P is

$$P = \frac{N!}{3!0!2!1!4!\dots}$$

We must take $0!$ equal to 1, since $n_i = 0$ can be chosen in only one way. The numbers n_1, n_2, n_3, \dots in Eq. (10.6) must be chosen in such a way that Eqs. (10.1) and (10.2), which give the total number of particles and the total energy, are satisfied.

So far we have assumed that all available states have the same probability of being occupied. It may happen that the states have different *intrinsic probabilities* g_i . For example, a certain energy state may be compatible with more different angular momentum states than other states, and therefore is more likely to be occupied. When this intrinsic probability is taken into account, the probability P of a given partition is slightly different from Eq. (10.6). Obviously, if g_i is the probability of finding a particle in the level of energy E_i , the probability of finding two particles in that level is $g_i \times g_i = g_i^2$, and for n_i particles it is $g_i \times g_i \times g_i \times \dots \times g_i = g_i^{n_i}$. Thus the total probability of a given partition, instead of being given by Eq. (10.6), is given by

$$P = \frac{N!g_1^{n_1}g_2^{n_2}g_3^{n_3}\dots}{n_1!n_2!n_3!\dots} \quad (10.7)$$

Finally let us remove the condition of distinguishability. If all particles are *identical and indistinguishable*, one cannot recognize the difference if, for example, in the partition in Fig. 10-1 particles a and p exchange places. Therefore all $N!$ permutations among the particles occupying the different states give the same partition. That means that we have to divide Eq. (10.7) by $N!$, resulting in

$$P = \frac{g_1^{n_1}g_2^{n_2}g_3^{n_3}\dots}{n_1!n_2!n_3!\dots} = \prod_{i=1}^N \frac{g_i^{n_i}}{n_i!} \quad \text{PB to all distinguishable particles} \quad \text{Maxwell-Boltzmann} \quad (10.8)$$

This is the expression for the probability of a distribution in Maxwell-Boltzmann statistics.

We can obtain the equilibrium state, corresponding to the most probable partition, by finding the maximum of P (given by Eq. 10.8) compatible with conditions (10.1) and (10.2), with N and U as constants. The method is a straightforward mathematical technique, and is explained in detail in Example 10.1. The result is that the partition having maximum probability is given by

$$n_i = g_i e^{-\alpha - \beta E_i} \quad (10.9)$$

where α and β are two parameters which, as will be shown, are related to the physical properties of the system. The quantity α may be expressed in terms of the total number of particles, N . Using Eq. (10.9), we have that

$$\begin{aligned} N &= n_1 + n_2 + n_3 + \dots \\ &= g_1 e^{-\alpha - \beta E_1} + g_2 e^{-\alpha - \beta E_2} + \dots \\ &= e^{-\alpha} (g_1 e^{-\beta E_1} + g_2 e^{-\beta E_2} + g_3 e^{-\beta E_3} + \dots) \\ &= e^{-\alpha} \left(\sum_i g_i e^{-\beta E_i} \right) = e^{-\alpha} Z, \end{aligned}$$

where

$$Z = \sum_i g_i e^{-\beta E_i} \quad \text{function PARTITION Z} \quad (10.10)$$

The quantity Z , called the *partition function*, is a very important expression which appears quite often in many calculations. We may thus write $e^{-\alpha} = N/Z$, and Eq. (10.9) becomes

$$n_i = \frac{N}{Z} g_i e^{-\beta E_i} \quad \text{LEGGE DI DISTR. DI MAXWELL-BOLTZMANN} \quad (10.11)$$

Expression (10.11) constitutes the *Maxwell-Boltzmann distribution law*. The quantity β is related to the energy of the system, or more precisely, to the average energy of a particle, as will be explained in Section 10.4.

We shall now illustrate an application of Eq. (10.11). From the definition of average value, we have that the average value (for a given partition) of a physical

property $F(E)$ that can be expressed as a function of the particle energy E is given by

$$F_{\text{ave}} = \frac{1}{N} \left[\sum_i n_i F(E_i) \right],$$

and for the most probable or equilibrium partition we have, using Eq. (10.11),

$$F_{\text{ave}} = \frac{1}{Z} \sum_i g_i F(E_i) e^{-\beta E_i}. \quad (10.12)$$

For example, if the particles of a system can be in only two states of energy, $E_1 = +\epsilon$ and $E_2 = -\epsilon$, both with the same probability ($g_1 = g_2 = 1$), then

$$Z = e^{-\beta E_1} + e^{-\beta E_2} = e^{-\beta \epsilon} + e^{\beta \epsilon} = 2 \cosh \beta \epsilon,$$

and the average energy of a particle is

$$\begin{aligned} E_{\text{ave}} &= \frac{1}{Z} (E_1 e^{-\beta E_1} + E_2 e^{-\beta E_2}) \\ &= \frac{\epsilon e^{-\beta \epsilon} - \epsilon e^{\beta \epsilon}}{2 \cosh \beta \epsilon} = -\epsilon \tanh \beta \epsilon. \end{aligned}$$

The total energy is

$$U = N E_{\text{ave}} = -N \epsilon \tanh \beta \epsilon.$$

which allows us to find β in terms of U .

EXAMPLE 10.1. Derivation of the most probable or equilibrium partition.

Solution: The most probable or equilibrium partition corresponds (by definition) to the maximum of P . This maximum, in turn, corresponds to the situation in which the change of P is practically zero ($dP = 0$) for small changes dn_1, dn_2, dn_3, \dots in the occupation numbers n_1, n_2, n_3, \dots . However, instead of obtaining the maximum of P , it is easier mathematically to obtain the maximum of $\ln P$, which corresponds to the same value of P . Now, from Eq. (10.9), we have

$$\begin{aligned} \ln P &= n_1 \ln g_1 + n_2 \ln g_2 + n_3 \ln g_3 + \dots \\ &\quad - \ln n_1! - \ln n_2! - \ln n_3! - \dots \end{aligned}$$

Using Stirling's formula for the logarithm of the factorial of a very large number (see Appendix V),

$$\ln x! \approx x \ln x - x,$$

and assuming that n_1, n_2, n_3, \dots are large numbers (since physical systems are in general composed of a great many particles), we have

$$\begin{aligned} \ln P &= n_1 \ln g_1 + n_2 \ln g_2 + n_3 \ln g_3 + \dots \\ &\quad - (n_1 \ln n_1 - n_1) - (n_2 \ln n_2 - n_2) - (n_3 \ln n_3 - n_3) - \dots \\ &= -n_1 \ln n_1/g_1 - n_2 \ln n_2/g_2 - \dots + (n_1 + n_2 + \dots), \end{aligned}$$

or, using Eq. (10.1), we may write

$$\ln P = N - \sum_i n_i \ln n_i/g_i. \quad (10.13)$$

Differentiating this expression (remembering that N is constant and thus $dN = 0$), we obtain

$$\begin{aligned} d(\ln P) &= - \sum_i (dn_i) \ln n_i/g_i - \sum_i n_i d(\ln n_i/g_i) \\ &= - \sum_i (dn_i) \ln n_i/g_i - \sum_i n_i (dn_i)/n_i \\ &= - \sum_i (dn_i) \ln n_i/g_i - \sum_i dn_i. \end{aligned} \quad (10.14)$$

But from Eq. (10.1), since $dN = 0$ because N is constant, we have

$$\sum_i dn_i = 0. \quad (10.15)$$

Therefore Eq. (10.14) reduces to

$$-d(\ln P) = \sum_i (\ln n_i/g_i) dn_i = 0. \quad (10.16)$$

We write zero on the right side of Eq. (10.16) because we are looking for the equilibrium state for which P is maximum, or $dP = 0$, and therefore $d(\ln P) = P^{-1} dP = 0$. If all the changes dn_1, dn_2, dn_3, \dots were arbitrary, we could satisfy Eq. (10.16) by making

$$\ln n_1/g_1 = 0, \ln n_2/g_2 = 0, \ln n_3/g_3 = 0, \dots \text{ or } n_1 = g_1, n_2 = g_2, \dots$$

However, the changes dn_i are not entirely arbitrary because of condition (10.15), which was derived from the constancy in the number of particles, and a similar condition,

$$\sum_i E_i dn_i = 0, \quad (10.17)$$

resulting from the constancy of the internal energy and obtained by differentiating Eq. (10.2) and setting $dU = 0$.

To compensate for the two conditions (10.15) and (10.17), we introduce two arbitrary parameters α and β , called *undetermined multipliers*, according to a mathematical technique suggested by Lagrange (see Appendix VII). Multiplying Eq. (10.15) by α , Eq. (10.17) by β , and adding these to Eq. (10.16), we obtain

$$\sum_i (\ln n_i/g_i + \alpha + \beta E_i) dn_i = 0.$$

This adds two new arbitrary coefficients α and β to compensate for the two restrictive conditions (10.15) and (10.17). The equilibrium distribution is then obtained if

$$\ln n_i/g_i + \alpha + \beta E_i = 0$$

or

$$n_i = g_i e^{-\alpha - \beta E_i},$$

which is the result previously stated in Eq. (10.9).

EXAMPLE 10.2. A system is composed of 4000 particles which may be in one of three energy states or levels, equally spaced, whose energies are 0, ϵ , and 2ϵ , all having the same intrinsic probability g (see Fig. 10-2). This system, for example, could consist of atoms whose total angular momentum is equal to 1, placed in a magnetic field. Compare the relative probabilities of the partition in which there are 2000 particles in the lower level, 1700 in the middle level, and 300 in the upper level with the partition resulting from the transfer of one particle from the middle level to the lower level and another to the upper level, a process compatible with the conservation of energy.

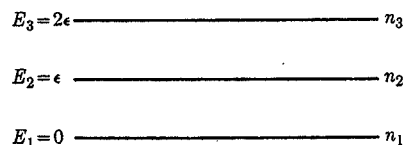


Fig. 10-2. System with three energy levels.

Solution: According to Eq. (10.8), the probabilities for the first and second partitions are

$$P_1 = \frac{g^{4000}}{2000!1700!300!}, \quad P_2 = \frac{g^{4000}}{2001!1698!301!}.$$

Instead of computing the values of P_1 and P_2 (which we could do by using Eq. 10.13), we shall simply find their ratios:

$$\frac{P_2}{P_1} = \frac{1700 \times 1699}{2001 \times 301} = \frac{2,888,300}{602,301} = 4.8.$$

Thus the mere transfer of two particles out of 4000 to other levels changes the probability by a factor of 4.8. This means that partitions P_1 and P_2 are both far from being the equilibrium partition; this situation is due to an excessive population of the middle level. Therefore the system will try to evolve to a state in which the middle level is less populated. It is suggested that the student repeat the problem, considering other possible distributions of particles, all compatible with the same total energy. (Shift two more particles from the middle level or move one particle from the upper level and another from the lower level into the middle level and recompute the relative probabilities.)

EXAMPLE 10.3. Determine the most probable or equilibrium partition for the system of Example 10.2.

Solution: The system is composed of $N = 4000$ particles, and according to the data given in Example 10.2, its total energy (see Fig. 10-2) is $2000 \times 0 + 1700 \times \epsilon + 300 \times (2\epsilon) = 2300\epsilon$. Using Eq. (10.9) for the most probable partition, we must have, according to the notation of Fig. 10-2, and with $g_1 = g_2 = g_3 = g$,

$$n_1 = ge^{-\alpha}, \quad n_2 = ge^{-\alpha-\beta\epsilon}, \quad n_3 = ge^{-\alpha-2\beta\epsilon}$$

or, if we designate $e^{-\beta\epsilon}$ by x , we have $n_2 = n_1x$ and $n_3 = n_1x^2$. Thus conditions (10.1) and (10.2), which give the total number of particles and the total energy, respectively, become

$$n_1 + n_1x + n_1x^2 = 4000, \quad (n_1x)\epsilon + (n_1x^2)(2\epsilon) = 2300\epsilon.$$

Canceling the common factor ϵ in the second relation, we have

$$\begin{aligned} n_1(1 + x + x^2) &= 4000, \\ n_1(x + 2x^2) &= 2300. \end{aligned}$$

Eliminating n_1 , we obtain an equation for x :

$$47x^2 + 17x - 23 = 0,$$

or $x = 0.5034$. (Only the positive root is used. Why?) Therefore $n_1 = 2277$ (the figure has been rounded). Accordingly, $n_2 = 1146$ and $n_3 = 577$. The corresponding partition probability is

$$P = \frac{g^{4000}}{2277!1146!577!}.$$

Let us now compute the change in P when two particles are removed from the intermediate level and transferred to the upper and lower levels. The new partition probability is

$$P' = \frac{g^{4000}}{2278!1144!578!}.$$

The ratio of the two probabilities is

$$\frac{P'}{P} = \frac{1146 \times 1145}{2278 \times 578} = \frac{1,312,170}{1,316,684} = 0.9966.$$

Therefore the two probabilities are essentially the same; this is as it should be, since, if P is a maximum, ΔP must be zero or very small for a small change in the distribution numbers of an equilibrium partition.

10.4 Temperature

The parameter β of Eqs. (10.10) and (10.11) is directly related to a physical quantity, the temperature, which was originally introduced more to describe a sensorial experience than a statistical property of an aggregate of particles. We first note that, if we are to have dimensional consistency in Eqs. (10.10) and (10.11), we must express β in reciprocal energy units; that is, J^{-1} , eV^{-1} , etc. Using Eq. (10.11), we have that the total energy of a system of particles in statistical equilibrium is

$$\begin{aligned} U &= n_1E_1 + n_2E_2 + n_3E_3 + \cdots \\ &= \frac{N}{Z} (g_1E_1e^{-\beta E_1} + g_2E_2e^{-\beta E_2} + g_3E_3e^{-\beta E_3} + \cdots) \end{aligned}$$

or

$$U = \frac{N}{Z} \left(\sum_i g_i E_i e^{-\beta E_i} \right) \quad (10.18)$$

Using the definition (10.10) of the partition function, we may write U in the alternative form

$$U = -\frac{N}{Z} \frac{d}{d\beta} \left(\sum_i g_i e^{-\beta E_i} \right) = -\frac{N}{Z} \frac{dZ}{d\beta} = -N \frac{d}{d\beta} (\ln Z), \quad (10.19)$$

which is an important relation between the total energy and the partition function of a system in statistical equilibrium. The average energy of a particle is

$$E_{\text{ave}} = \frac{U}{N} = -\frac{d}{d\beta} (\ln Z). \quad (10.20)$$

Note that, given a physical system described by the g_i 's and the E_i 's, the partition function Z (and hence the total energy U) as well as the average energy of a particle, E_{ave} , are functions of β (and also other parameters which determine the macroscopic state, such as volume and pressure). That is, we may use the parameter β to characterize the internal energy of the system. However, it has been found more convenient to introduce a new physical quantity instead of β . This quantity is called the absolute temperature of the system; it is designated by T , and defined according to the relation

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$$kT = \frac{1}{\beta} \quad \rightarrow \quad \text{dalla Maxwelliana} \quad \left\{ \begin{array}{l} dn = A \sqrt{E} e^{-E/kT} dE \\ n_i = \frac{1}{Z} g_i e^{-\beta E_i} \end{array} \right\} \quad \beta = \frac{1}{kT} \quad (10.21)$$

The quantity kT must obviously be expressed in units of energy, such as joules or electron volts. The constant k is called the Boltzmann constant. Its value is determined after the units for T are chosen. It remains to be shown that the temperature we have defined here coincides with the temperature as measured by, say, a gas thermometer. We shall do this later on (Section 12.2). At this time it is enough to say that when T is expressed in a unit called degrees kelvin, designated by $^\circ\text{K}$ (which was introduced before statistical mechanics was developed), the value of the Boltzmann constant is

$$k = 1.3805 \times 10^{-23} \text{ J } ^\circ\text{K}^{-1} = 8.6178 \times 10^{-5} \text{ eV } ^\circ\text{K}^{-1}.$$

Of course, we could make $k = 1$ and measure the temperature directly in energy units, such as joules or electron volts. This is perfectly possible. However, the tradition of expressing temperature in degrees, introduced long before the relation between temperature and the molecular structure of a system was recognized, is so well entrenched in physics that it is almost impossible (and perhaps also undesirable) to do away with the use of degrees. The quantity β is positive (except in some special cases), as will be shown later; hence the absolute temperature T is positive. The lowest temperature is zero, which corresponds to what is called absolute zero.

It must be clearly kept in mind that the statistical definition of temperature, as given by Eq. (10.21), is valid only for a system of particles in statistical equilibrium, and hence does not apply to a single particle or to a system which is not in

equilibrium. The reason for this is that the parameter β appears only in connection with the calculation of the most probable partition of a system, which corresponds, by definition, to the equilibrium state. If the system is not in equilibrium, we may still speak of an "effective" temperature of each small portion of the system, assuming that each small portion is almost in equilibrium.

When we introduce the definition (10.21) of temperature in Eq. (10.10), we may write the equilibrium partition function as

$$Z = \sum_i g_i e^{-E_i/kT}. \quad (10.22)$$

Similarly, the equilibrium occupation numbers are given by

$$n_i = \frac{N}{Z} g_i e^{-E_i/kT}, \quad (10.23)$$

which gives the Maxwell-Boltzmann distribution law in terms of the temperature. Since $\beta = 1/kT$, then $d\beta = -dT/kT^2$, and we can write Eq. (10.19) as

$$U = kNT^2 \frac{d}{dT} (\ln Z). \quad (10.24)$$

The average energy per particle, U/N , is given by

$$E_{\text{ave}} = kT^2 \frac{d}{dT} (\ln Z). \quad (10.25)$$

Note that Eq. (10.25) establishes a relation between the average energy per particle of a system in statistical equilibrium and the temperature of the system. The exact relation obviously depends on the microscopic structure of the system, which is expressed in the partition function Z , and is different for an ideal gas, a real gas, a liquid, or a solid. Hence we may say that the temperature of a system in statistical equilibrium is a quantity related to the average energy per particle of the system, the relation depending on the structure of the system.

In the general case, the average value of any particle property, $F(E)$, which was defined in Eq. (10.12), now becomes

$$F_{\text{ave}} = \frac{1}{Z} \sum_i g_i F(E_i) e^{-E_i/kT}, \quad (10.26)$$

and is thus a function of the temperature. For example, for the system composed of particles of energies $+\epsilon$ and $-\epsilon$, considered at the end of Section 10.3, the average energy of a particle at the temperature T is

$$E_{\text{ave}} = -\epsilon \tanh(\epsilon/kT).$$

Since the exponential $e^{-E_i/kT}$ in Eq. (10.23) is a decreasing function of E_i/kT , the larger the ratio E_i/kT , the smaller the value of the occupation number n_i . Therefore, at a given temperature, the larger the energy E_i , the smaller the value

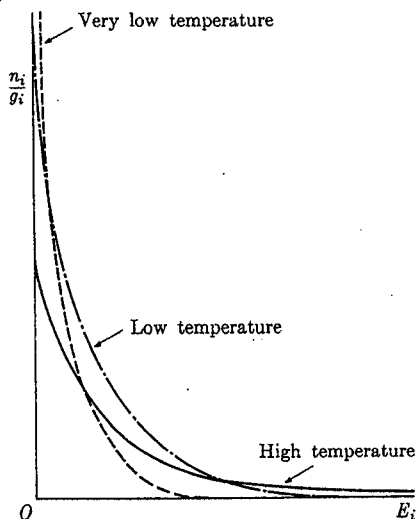
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of n_i . In other words, the occupation of states available to the particles decreases as their energy increases. At very low temperatures only the lowest energy levels are occupied, as shown in Fig. 10-3; but at higher temperatures (corresponding to smaller values of E_i/kT for a given energy) the relative population of the higher energy levels increases (again as shown in Fig. 10-3) by transfer of particles from lower to higher energy levels. At the absolute zero of temperature, only the ground or lowest energy level is occupied. Note that the relation of the occupation numbers between two energy levels E_i and E_j is

$$\frac{n_j}{n_i} = \frac{g_j}{g_i} e^{-(E_j - E_i)/kT} = \frac{g_j}{g_i} e^{-\Delta E/kT}, \quad (10.27)$$

where ΔE is the energy difference between the two levels. Thus n_i and n_j are comparable only if ΔE is much smaller than kT .

Fig. 10-3. Maxwell-Boltzmann distribution at three different temperatures.



EXAMPLE 10.4. Given temperatures of 100°K, 300°K (room temperature), and 1000°K, determine for each temperature the ratio between the occupation numbers for two levels corresponding to ΔE equal to: (a) 10^{-4} eV, which is a value equivalent to the spacing of rotational levels for many molecules, (b) 5×10^{-2} eV, which corresponds to molecular vibrational levels, and (c) 3.00 eV, which is of the order of magnitude of electronic excitation of atoms and molecules. Assume $g = 1$.

Solution: Remembering that $k = 8.6178 \times 10^{-5}$ eV °K $^{-1}$, we have that $kT = 8.6178 \times 10^{-5}T$ eV, and $\Delta E/kT = 1.1603 \times 10^4 \Delta E/T$, where ΔE is expressed in electron volts. Therefore, for the indicated values of ΔE , the values of n_j/n_i at the three temperatures are as given in the following table.

ΔE , eV	100°K	300°K	1000°K
10^{-4}	0.9885	0.9962	0.9988
5×10^{-2}	3×10^{-3}	1.45×10^{-1}	5.60×10^{-1}
3.00	3×10^{-164}	8×10^{-49}	8×10^{-16}

Therefore, for $\Delta E = 10^{-4}$ eV, the two levels are practically equally populated at all temperatures considered. This explains, for example, why the complete rotational ab-

sorption spectrum of molecules is observed at normal temperature, as illustrated in Fig. 5-35 for HCl. At $\Delta E = 5 \times 10^{-2}$ eV, the population of the upper level is already appreciable at room temperature, which means that many molecules are in an excited vibrational state at room temperatures. However, for $\Delta E = 3$ eV, the ratio n_j/n_i is so small that it is plausible to consider the upper level as essentially empty at all temperatures considered. Thus most atoms and molecules (at room temperature) are in their ground electronic state. Only at extremely high temperatures, as in very hot stars, are there atoms and molecules in excited electronic states in any appreciable amount. In the laboratory, electronic excitations are produced by means of inelastic collisions of gas molecules with fast electrons in an electric discharge.

EXAMPLE 10.5. Consider a system of polar molecules which are placed in a uniform electric field, but which are otherwise isolated from any other external action. Compute the polarization of the system as a function of the temperature.

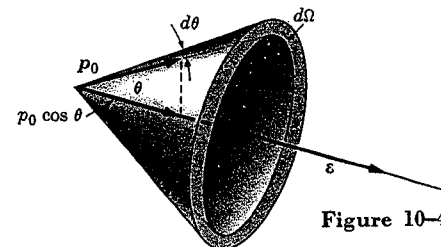
Solution: Let us designate the electric dipole moment of each molecule by p_0 . We shall assume that the effect of the applied electric field is only to modify the random orientation of the molecules without disturbing their translational or internal (rotational or vibrational) motions, and that the molecules are free to follow the orienting action of the electric field. The energy of a molecule whose dipole moment makes an angle θ with the electric field \mathcal{E} is $E(\theta) = -p_0\mathcal{E} \cos \theta$. Since the angle θ can have any value between 0 and π , the energies of the available states are not discrete but vary continuously. Thus, instead of looking for the number of molecules oriented at an angle θ , we must find the number of molecules with their dipoles oriented within the solid angle $d\Omega$, defined as being between cones of angles θ and $\theta + d\theta$ (Fig. 10-4). The value of this solid angle is $d\Omega = 2\pi \sin \theta d\theta$, and using Eq. (10.22) with g_i replaced by $d\Omega$ and the summation replaced by an integral, we may write the partition function as

$$Z = \int_0^\pi e^{p_0\mathcal{E} \cos \theta / kT} 2\pi \sin \theta d\theta = 4\pi(kT/p_0\mathcal{E}) \sinh(p_0\mathcal{E}/kT).$$

The orientation of the molecules must be symmetric relative to the direction of the electric field and the average value of their electric dipole moment is parallel to \mathcal{E} . Thus, to find p_{ave} , we must evaluate $(p_0 \cos \theta)_{\text{ave}}$, since $p_0 \cos \theta$ is the component of the electric dipole moment in the direction of \mathcal{E} . Using Eq. (10.26), with the summation replaced by an integral, we have

$$p_{\text{ave}} = \frac{1}{Z} \int_0^\pi (p_0 \cos \theta) e^{p_0\mathcal{E} \cos \theta / kT} 2\pi \sin \theta d\theta$$

$$= p_0 \left(\coth \frac{p_0\mathcal{E}}{kT} - \frac{kT}{p_0\mathcal{E}} \right),$$



a result which is called Langevin's formula. At very large \mathcal{E} or very small temperature (that is, for $p_0\mathcal{E} \gg kT$), we have that $\coth(p_0\mathcal{E}/kT) \rightarrow 1$ and $kT/p_0\mathcal{E} \rightarrow 0$, so that $p_{\text{ave}} = p_0$. This means that for a very large electric field, or at temperatures near absolute zero, practically all molecules are oriented parallel to the electric field. For small \mathcal{E}

or large T (that is, $p_0\epsilon/kT \ll 1$), we use the asymptotic expansion

$$\coth x = 1/x + x/3 + \dots,$$

and thus

$$p_{\text{ave}} = p_0\epsilon/3kT.$$

If there are n molecules per unit volume, the polarization of the substance is

$$\mathcal{P} = np_{\text{ave}} = (np_0^2/3kT)\epsilon.$$

This expression is used in the calculation of the electric permittivity of a medium composed of polar molecules. The magnetization of a substance placed in an external magnetic field when the molecules have a permanent magnetic moment is obtained by a similar calculation. This is the orientation effect which gives rise to paramagnetism. In this case, however, a complication arises. The magnetic moment is related to the angular momentum, which is restricted in orientation, as indicated in Section 3.4. Thus instead of performing an integration, we must perform a summation. The final result is still very similar to that obtained for an electric dipole moment (see Problem 10.8).

10.5 Thermal Equilibrium

Consider a system composed of two different groups of particles. We shall say that each group of particles constitutes a subsystem. Our two subsystems may, for example, consist of a liquid with a solid immersed in it, a mixture of two gases or liquids, or two solids in contact. By means of collisions and other interactions, energy may be exchanged between the particles composing the two subsystems, but the total energy of the whole system is assumed to be fixed. Let us designate the total numbers of particles in each subsystem by N and N' and the corresponding energy levels available to the particles by E_1, E_2, E_3, \dots and E'_1, E'_2, E'_3, \dots . If there are no reactions between the particles in the two subsystems, the total number of particles in each subsystem is constant; also the total energy of the system is constant. But the energy of each subsystem is not conserved because, due to their interactions, energy may be exchanged between them. Therefore the following conditions for the two subsystems must be fulfilled by the occupation numbers n_1, n_2, n_3, \dots , and n'_1, n'_2, n'_3, \dots in a given partition:

$$N = \sum_i n_i = \text{const}, \quad (10.28)$$

$$N' = \sum_j n'_j = \text{const}, \quad (10.29)$$

$$U = \sum_i n_i E_i + \sum_j n'_j E'_j = \text{const}. \quad (10.30)$$

The probability of a given partition or distribution is given by the product of two expressions similar to Eq. (10.8), one for each subsystem:

$$P = \left[\frac{g_1^{n_1} g_2^{n_2} g_3^{n_3} \dots}{n_1! n_2! n_3! \dots} \right] \times \left[\frac{g'_1{}^{n'_1} g'_2{}^{n'_2} g'_3{}^{n'_3} \dots}{n'_1! n'_2! n'_3! \dots} \right]. \quad (10.31)$$

We can obtain the equilibrium of the composite system by requiring that P be a maximum, compatible with Eqs. (10.28), (10.29), and (10.30). The result (see Example 10.6) is that

$$\left[n_i = \frac{N}{Z} g_i e^{-\beta E_i}, \quad n'_j = \frac{N'}{Z'} g'_j e^{-\beta E'_j} \right] \quad (10.32)$$

where Z and Z' are the respective partition functions of the two subsystems. We also note that the two subsystems in equilibrium must have the same parameter β . In view of our definition of temperature, Eq. (10.21), we conclude that

two different and interacting systems of particles in statistical equilibrium must have the same temperature. LEG
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a statement called the zeroth law of thermodynamics. It is then said that the subsystems are in thermal equilibrium. Hence, when we replace β by $1/kT$, instead of Eq. (10.32) we may write

$$n_i = \frac{N}{Z} g_i e^{-E_i/kT}, \quad n'_j = \frac{N'}{Z'} g'_j e^{-E'_j/kT},$$

where T is the common absolute temperature of the two subsystems. The expressions for n_i and n'_j show that at thermal equilibrium each subsystem attains the same most probable partition as if it were isolated and at the same temperature T . These relations therefore express the fact that, in a statistical sense, after thermal equilibrium is attained the energy of each subsystem remains constant. This means that, although both systems may exchange energy at the microscopic level, the exchange takes place in both directions and, on the average, no net energy is exchanged in either direction. Therefore, statistically, the energy of each subsystem remains constant. It then follows that when two bodies at different temperatures are placed in contact they will exchange energy until both reach thermal equilibrium at the same temperature. At this point no further net exchange of energy takes place.

The zeroth law is the basis of the measurement of the temperature of a body; this temperature is determined by placing it in contact with a properly calibrated standard body (or thermometer). The zeroth law is also in agreement with our common understanding of the concept of temperature by which, if a "cold" and a "hot" body are placed in contact, the cold warms up and the hot cools off until both are "felt" at the same temperature. Therefore, although the concept of temperature was first introduced to correspond to a sensorial experience which is, of course, associated with a physical condition of the human body, it can now be defined precisely by means of the statistical relation (10.21).

EXAMPLE 10.6. Derivation of relations (10.32).

Solution: When P is given by Eq. (10.31), if we follow the same procedure used to obtain Eq. (10.16), we have

$$-d(\ln P) = \sum_i \ln n_i / g_i \, dn_i + \sum_j \ln n'_j / g'_j \, dn'_j = 0. \quad (10.33)$$

The restricting conditions (10.28), (10.29), and (10.30) now give

$$\sum_i dn_i = 0, \quad (10.34)$$

$$\sum_j dn'_j = 0, \quad (10.35)$$

$$\sum_i E_i dn_i + \sum_j E'_j dn'_j = 0. \quad (10.36)$$

Multiplying Eq. (10.34) by α , Eq. (10.35) by α' , and Eq. (10.36) by β , and introducing these in Eq. (10.33), we get

$$\sum_i (\ln n_i/g_i + \alpha + \beta E_i) dn_i + \sum_j (\ln n'_j/g'_j + \alpha' + \beta E'_j) dn'_j = 0,$$

which requires (for the same reason as in the case of only one kind of particle) that

$$\ln n_i/g_i + \alpha + \beta E_i = 0, \quad \ln n'_j/g'_j + \alpha' + \beta E'_j = 0.$$

Accordingly we get

$$n_i = g_i e^{-\alpha - \beta E_i}, \quad n'_j = g'_j e^{-\alpha' - \beta E'_j}$$

or, using relations (10.28) and (10.29) to eliminate $e^{-\alpha}$ and $e^{-\alpha'}$

$$n_i = \frac{N}{Z} g_i e^{-\beta E_i}, \quad n'_j = \frac{N'}{Z'} g'_j e^{-\beta E'_j}.$$

Note that we use α and α' because the number of particles of each subsystem is conserved separately, but we use only one β because it is the total energy which is conserved.

10.6 Application to the Ideal Gas

Our next step is to determine whether there is any system of particles in nature whose collective behavior resembles the predictions of the Maxwell-Boltzmann distribution law. Up to this point we have presented this distribution only as a more or less reasonable theoretical construction. Experience confirms the fact that most gases can be described according to Maxwell-Boltzmann statistics over a wide range of temperature. For simplicity we shall now consider ideal gases composed of monatomic molecules. In this way we do not have to include the potential energy due to the intermolecular forces nor the energy associated with internal rotational or vibrational motions of the molecules, and all molecular energy is translational kinetic; that is, E_i in Eq. (10.11) is

$$E_i = \frac{1}{2m} p_i^2 = \frac{1}{2} m v_i^2. \quad (10.37)$$

But we note, as explained in Example 2.6, that the kinetic energy of an ideal gas occupying a rather large volume may be considered as not being quantized but as having a continuous spectrum. Therefore we must rewrite Eq. (10.22), replacing

the sum by an integral in the form

$$Z = \int_0^\infty e^{-E/kT} g(E) dE, \quad (10.38)$$

where $g(E) dE$ replaces g_i and represents the number of molecular states in the energy range between E and $E + dE$. This number arises from the different orientations of the momentum p for a given energy. From Eq. (2.49) of Example 2.4 we have that

$$g(E) dE = \frac{4\pi V (2m^3)^{1/2}}{h^3} E^{1/2} dE, \quad (10.39)$$

where V is the volume occupied by the gas. Therefore

$$Z = \frac{4\pi V (2m^3)^{1/2}}{h^3} \int_0^\infty E^{1/2} e^{-E/kT} dE. \quad \int_0^\infty x^2 e^{-ax^2} dx = \frac{1}{4} \sqrt{\frac{\pi}{a^3}} \quad \text{from } \int_0^\infty x^2 e^{-ax^2} dx = \frac{1}{2a} \int_0^\infty x e^{-ax^2} dx = \frac{1}{2a} \left[-\frac{1}{2a} e^{-ax^2} \right]_0^\infty = \frac{1}{4a^2}$$

The integral appearing on the right can be found (see Appendix IV) to have the value $\frac{1}{2} \sqrt{\pi (kT)^3}$. Therefore

$$Z = \frac{V (2\pi m kT)^{3/2}}{h^3}, \quad (10.40)$$

which gives the partition function of an ideal monatomic gas as a function of the temperature and the volume of the gas. Then, by taking the natural logarithm of each side, we have

$$\ln Z = C + \frac{3}{2} \ln kT,$$

where C includes all the remaining constant quantities. Substituting this value of $\ln Z$ in Eq. (10.25), we obtain the average energy of the molecules as

$$E_{\text{ave}} = kT^2 \frac{d \ln Z}{dT} = E_{\text{ave}} = \frac{3}{2} kT. \quad (10.41)$$

Therefore the average kinetic energy of the molecules of an ideal gas in statistical equilibrium is proportional to the absolute temperature of the gas. Historically, Eq. (10.41) was introduced in the nineteenth century, long before the development of statistical mechanics, in connection with the kinetic theory of gases. It was this relation that suggested the identification of β with $1/kT$. The total energy of a gas composed of N molecules is then

$$U = N E_{\text{ave}} = \frac{3}{2} kNT.$$

We conclude then that the internal energy of an ideal monatomic gas depends only on its temperature. This is a direct result of our definitions of an ideal gas and of temperature. We do not expect the same relations to hold for real gases or other substances, since their internal energy is partly potential and thus depends on the separation of the molecules; that is, on the volume of the substance.

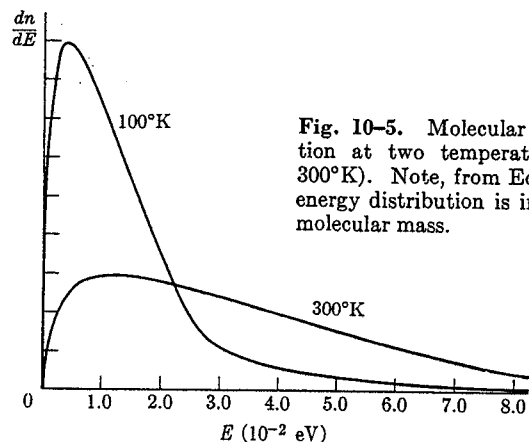


Fig. 10-5. Molecular energy distribution at two temperatures (100°K and 300°K). Note, from Eq. (10.44), that the energy distribution is independent of the molecular mass.

If N is the number of moles* of the gas, and $N_A = 6.0225 \times 10^{23} \text{ mole}^{-1}$ is Avogadro's constant, which is the number of molecules in one mole of the substance and which is the same for all substances, we have $N = N/N_A$. Thus

$$U = \frac{3}{2} N k N_A T = \frac{3}{2} N R T, \quad (10.42)$$

where

$$\begin{aligned} R &= k N_A = \frac{8.3143 \text{ J mole}^{-1} \text{ }^\circ\text{K}^{-1}}{1.9860 \text{ calories mole}^{-1} \text{ }^\circ\text{K}^{-1}} \\ &= 5.1894 \times 10^{19} \text{ eV mole}^{-1} \text{ }^\circ\text{K}^{-1} \end{aligned} \quad (10.43)$$

is called the gas constant.

Expression (10.23) for the distribution of molecules among the different energies, with g_i replaced by $g(E) dE$ as given by Eq. (10.39), is now

$$\left[dn = \frac{N}{Z} e^{-E/kT} g(E) dE = \frac{N}{Z} \frac{4\pi V (2m^3)^{1/2}}{h^3} E^{1/2} e^{-E/kT} dE \right]$$

where dn is the number of molecules with energy between E and $E + dE$. By introducing the value of Z as given by Eq. (10.40), we have

$$\frac{dn}{dE} = \frac{2\pi N}{(\pi kT)^{3/2}} E^{1/2} e^{-E/kT}, \quad (10.44)$$

which is Maxwell's formula for the energy distribution of the molecules in an ideal gas. This constitutes one of the earliest applications of statistical methods in physics. It was originally derived by James C. Maxwell around 1857, using a different logic. A plot of Eq. (10.44) for two different temperatures is represented in Fig. 10-5.

* Recall that one mole of a substance is an amount of that substance, in grams, equal to its molecular mass expressed in amu.

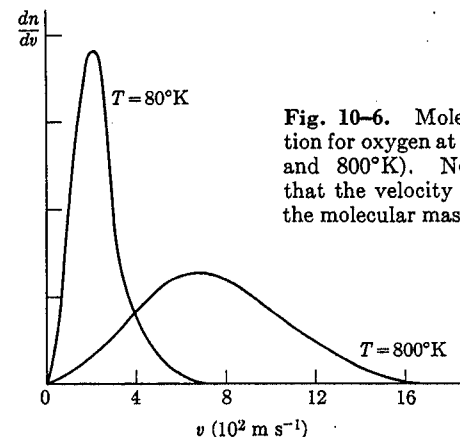


Fig. 10-6. Molecular velocity distribution for oxygen at two temperatures (80°K and 800°K). Note, from Eq. (10.45), that the velocity distribution depends on the molecular mass.

Sometimes we require the velocity distribution rather than the energy distribution. Noting that $E = \frac{1}{2} m v^2$, we then have that

$$\frac{dn}{dv} = \frac{dn}{dE} \frac{dE}{dv} = m v \frac{dn}{dE}.$$

Making the substitution $E = \frac{1}{2} m v^2$ in Eq. (10.44), we get

$$\frac{dn}{dv} = 4\pi N \left(\frac{m}{2\pi kT} \right)^{3/2} v^2 e^{-mv^2/2kT}, \quad (10.45)$$

which is Maxwell's formula for the velocity distribution of the molecules in an ideal gas. It gives the number of molecules moving with a velocity between v and $v + dv$, irrespective of the direction of motion. The velocity distribution for oxygen at two different temperatures is represented in Fig. 10-6.

A crucial test of the applicability of Maxwell-Boltzmann statistics to ideal gases is to see whether the energy and velocity distributions illustrated in Figs. 10-5 and 10-6 actually occur. One indirect way of doing this is to analyze the dependence of the rate of chemical reactions on the temperature. Suppose that a particular reaction occurs only if the colliding molecules have a certain energy equal to or larger than E_a . The rate of reaction at a given temperature then depends on the number of molecules having an energy equal to or larger than E_a . These numbers, for two different temperatures, are given by the shaded areas under the low-temperature and high-temperature curves of Fig. 10-7. We note that there are more molecules available at high than at low temperatures. By proper calculation, we can predict the effect of these additional molecules, and the theoretical prediction can be compared with the experimental data. Experimental results are in excellent agreement with Eq. (10.45); this confirms the applicability of Maxwell-Boltzmann statistics to gases.

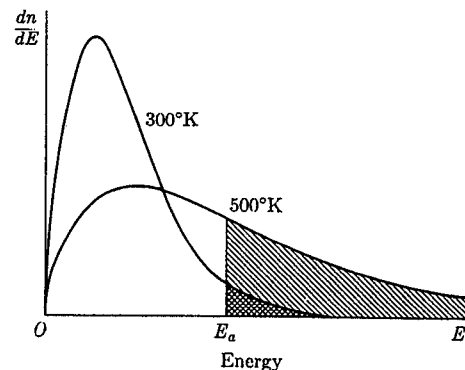


Fig. 10-7. Number of molecules with energy larger than E_a at two different temperatures. The number in each case is indicated by the shaded area.

^uCHOPPER" A more direct verification would consist in an actual "count" of the number of molecules in each energy or velocity interval. Several experimental arrangements have been used for this purpose. One method, using a velocity selector or "chopper," is illustrated in Fig. 10-8. The two slotted disks, D and D' , rotate with an angular velocity ω and their slots are displaced by an angle θ . When gas molecules escape from an oven at a certain temperature (a process called *effusion*), they pass through both slots and are received at the detector only if their velocity is $v = s\omega/\theta$. Actually, since the slots have a finite width, the transmitted molecules have velocities in a certain range Δv about the given value. When either ω or θ is changed, the velocity of the molecules received at the detectors can be changed. If one makes several observations for different velocities v , the velocity and energy distributions are obtained. The experimental results confirm the prediction of Maxwell-Boltzmann statistics, as expressed by Eqs. (10.44) and (10.45).

As explained in Section 8.6, neutrons produced in the fission process in a nuclear reactor are slowed down by means of a suitable moderator until they are in thermal

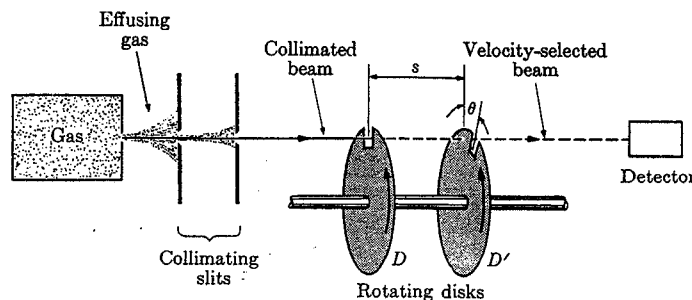


Fig. 10-8. Molecular velocity selector.

equilibrium at the temperature of the reactor. Neutrons in a thermal nuclear reactor then behave as an ideal gas and their energy distribution agrees with Maxwell's law, Eq. (10.44); that is, thermal neutrons follow Maxwell-Boltzmann statistics. This fact is essential in nuclear reactor design. If the neutrons emerging from a porthole in a reactor are made to pass through a chopper similar to that of Fig. 10-8, a monoenergetic beam of neutrons is obtained.

EXAMPLE 10.7. Obtain the most probable energy and velocity of the gas molecules at a given temperature; these values correspond to the maxima of dn/dE and dn/dv , respectively.

Solution: To obtain the maximum of dn/dE , given by Eq. (10.44), at a certain temperature, it is necessary to compute only the maximum of $y = E^{1/2}e^{-E/kT}$. Thus

$$\frac{dy}{dE} = \left(\frac{1}{2}E^{-1/2} - \frac{E^{1/2}}{kT} \right) e^{-E/kT} = 0,$$

from which we have $E_{mp} = \frac{1}{2}kT$. Thus at room temperature, for which $kT \sim 0.025$ eV, we have $E_{mp} \sim 0.012$ eV.

Similarly, to obtain the maximum of dn/dv , given by Eq. (10.45), we must compute the maximum of $y = v^2 e^{-mv^2/2kT}$. Then

$$\frac{dy}{dv} = \left(2v - \frac{mv^3}{kT} \right) e^{-mv^2/2kT} = 0.$$

Therefore $v_{mp} = \sqrt{2kT/m}$. This velocity corresponds to an energy $E = kT$ and is therefore different from E_{mp} . Can the student explain the reason for this difference?

EXAMPLE 10.8. Average velocity (v_{ave}) and root-mean-square velocity (v_{rms}) of the molecules in an ideal gas.

Solution: The average velocity is defined by

$$v_{ave} = \frac{1}{N} \int_0^\infty v \, dn = \frac{1}{N} \int_0^\infty v \frac{dn}{dv} dv.$$

Introducing the value of dn/dv given by Eq. (10.45), we have

$$v_{ave} = 4\pi \left(\frac{m}{2\pi kT} \right)^{3/2} \int_0^\infty v^3 e^{-mv^2/2kT} dv.$$

We first transform the integral by setting $u = v^2$, so that $du = 2v \, dv$, resulting in

$$\frac{1}{2} \int_0^\infty u e^{-(m/2kT)u} du.$$

Next we integrate by parts, resulting in $\frac{1}{2}(2kT/m)^2$, so that

$$v_{ave} = \left(\frac{8kT}{\pi m} \right)^{1/2} = \left(\frac{2.55kT}{m} \right)^{1/2} = 1.13v_{mp}.$$

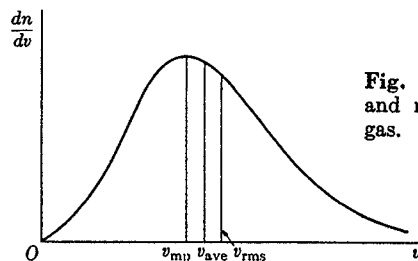


Fig. 10-9. Most probable, average, and root-mean-square velocities of a gas.

We define the root-mean-square velocity by $v_{\text{rms}}^2 = (v^2)_{\text{ave}}$, and we obtain the average of v^2 from the expression

$$(v^2)_{\text{ave}} = \frac{1}{N} \int_0^{\infty} v^2 dn.$$

Noting that $v^2 = 2E/m$, we may also write

$$(v^2)_{\text{ave}} = \frac{2}{m} \frac{1}{N} \int_0^{\infty} E dn = \frac{2}{m} E_{\text{ave}},$$

since the average energy is defined by $E_{\text{ave}} = (1/N) \int E dn$. But for an ideal gas, according to Eq. (10.44), $E_{\text{ave}} = \frac{3}{2} kT$. Thus

$$v_{\text{rms}}^2 = (v^2)_{\text{ave}} = \frac{2}{m} \left(\frac{3}{2} kT \right) = \frac{3kT}{m}$$

and

$$v_{\text{rms}} = \left(\frac{3kT}{m} \right)^{1/2} = 1.25 v_{\text{mp}}.$$

The three velocities, v_{mp} , v_{ave} , and v_{rms} are indicated in Fig. (10-9).

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Problems

10.1 Referring to Example 10.2, find the change in the probability of the distribution if two particles, one from the upper and one from the lower level, are transferred to the intermediate level. Repeat for the most probable partition found in Example 10.3.

10.2 In Example 10.2, compute the ratio P_2/P_1 , using Eq. (10.13) for $\ln P$.

10.3 Determine the temperature of the system of Example 10.3 when it is in statistical equilibrium. Assume $\epsilon = 0.02$ eV.

10.4 Find the ratio of the number of electrons having their spins parallel and antiparallel to a magnetic field as a function of the temperature. Evaluate the number for a temperature T equal to 10° , 300° , and 1000°K . [Hint: Recall that the spin magnetic moment of the electrons is given by $M_s = -2\mu_B S$, Eq. (3.33).]

10.5 (a) Show that the partition function of an electron gas placed in a magnetic field \mathcal{B} is $Z = 2 \cosh(\mu_B \mathcal{B}/kT)$, where μ_B is a Bohr magneton. (b) Compute the magnetic energy of an electron gas in the magnetic field; then show that the paramagnetism of free electrons corresponds to a magnetization $M = n\mu_B \tanh(\mu_B \mathcal{B}/kT)$, where n is the number of electrons per unit volume. (c) Find the limiting values of the partition function and the magnetization at very low and very high temperatures.

10.6 The possible particle energies of a system of particles are $0, \epsilon, 2\epsilon, \dots, n\epsilon, \dots$ (a) Show that the partition function of the

system (with $g_i = 1$) is

$$Z = (1 - e^{-\epsilon/kT})^{-1}.$$

(b) Compute the average energy of the particles. (c) Find the limiting value of the average energy when ϵ is much smaller than kT .

10.7 Considering a system of particles having energies $0, \epsilon, 2\epsilon, \dots, n\epsilon, \dots$, plot a graph showing the occupation numbers for (a) 100°K , (b) 300°K , (c) 800°K , given that the value of the energy ϵ is (a) 10^{-3} eV, (b) 0.1 eV. [Hint: Use the result of Problem 10.6 for the partition function.]

10.8 The magnetic moment of atoms (or molecules) having an angular momentum J is given by Eq. (3.40): $M = -\mu_B g J$. (a) Obtain an expression giving the number of atoms having a value of J_z equal to $m\hbar$, if the atoms are placed in a magnetic field \mathcal{B} oriented parallel to the Z -axis. (b) Show that the partition function of the system of atoms is

$$Z = \frac{\sinh[(j + \frac{1}{2})\mu_B g \mathcal{B}/kT]}{\sinh[\frac{1}{2}\mu_B g \mathcal{B}/kT]}$$

(c) Verify that for $j = \frac{1}{2}$ the partition function reduces to that obtained for electrons in Problem 10.5.

10.9 Obtain the average magnetic energy of the atoms considered in the preceding problem. Verify from this result that the average magnetic moment of the atoms in a direction parallel to the magnetic field is

$$M_{\text{ave}} = \mu_B g [(j + \frac{1}{2}) \coth(j + \frac{1}{2})x - \frac{1}{2} \coth \frac{1}{2}x]$$

where $x = \mu_{\text{B}}g/kT$. Find the limiting values of M_{ave} for x very small and very large compared with 1.

10.10 At what temperature is the number of molecules of an ideal gas per unit energy range at 2×10^{-2} eV, one-fourth of the number corresponding to 1×10^{-2} eV?

10.11 Find the ratio of the number of molecules of an ideal gas per unit energy range at energies of 0.2 eV and 0.02 eV, given that the gas temperature is (a) 100°K, (b) 300°K, (c) 600°K.

10.12 Compute enough points to construct graphs of the molecular energy distribution function in an ideal gas for one kilomole at 200°K and 600°K.

10.13 (a) Compute the root-mean-square, average, and most probable velocities of oxygen molecules at a temperature of 300°K. (b) Compute the most probable velocity of oxygen molecules at the following temperatures: 100°K, 300°K, 1000°K, 10,000°K.

10.14 (a) Compute the mean translational kinetic energy of an ideal gas molecule at 300°K. (b) Compute the root-mean-square velocity if the gas is hydrogen (H_2), oxygen (O_2), or mercury vapor (Hg). Compare your results for hydrogen and oxygen with the velocity of sound in those gases.

10.15 Compute the root-mean-square velocity of (a) helium atoms at 2°K, (b) nitrogen molecules at 27°C, (c) mercury atoms at 100°C.

10.16 At what temperature is the mean translational kinetic energy of a molecule of an ideal gas equal to that of a singly charged ion of the same mass that has been accelerated from rest through a potential difference of (a) 1 volt, (b) 1000 volts, (c) 1,000,000 volts? Neglect relativistic effects.

10.17 Determine the fractional number of molecules of an ideal gas with velocities between v_{ave} and $1.2v_{\text{ave}}$ from Eq. (10.45) making (a) $v = v_{\text{ave}}$ and $dv = 0.2v_{\text{ave}}$; (b) $v = 1.1v_{\text{ave}}$ and $dv = 0.2v_{\text{ave}}$.

10.18 Show that the number of molecules of an ideal gas moving with velocity having components in the range v_x and $v_x + dv_x$, v_y and $v_y + dv_y$, v_z and $v_z + dv_z$, is given by

$$dn = N(m/2\pi kT)^{3/2} e^{-mv^2/2kT} dv_x dv_y dv_z.$$

[Note that, in Eq. (10.45), for this case we must replace the integration element $4\pi v^2 dv$ by $dv_x dv_y dv_z$. Justify this replacement.]

10.19 Show that the number of molecules of an ideal gas that have an X -component of velocity between v_x and $v_x + dv_x$ irrespective of the values of the v_y and v_z components is

$$dn = N(m/2\pi kT)^{1/2} e^{-mv_x^2/2kT} dv_x.$$

[Hint: Integrate the expression obtained in Problem 10.18 over v_y and v_z . The limits of integration in each case must be from $-\infty$ to $+\infty$.]

10.20 Use the result of Problem 10.19 to obtain the average value of (a) v_x , (b) v_x^2 , (c) $|v_x|$ for an ideal gas.

10.21 The error function $\text{erf}(x)$ is defined by

$$\text{erf}(x) = \frac{1}{\sqrt{\pi}} \int_0^x e^{-x^2} dx.$$

In Table 10-1 we give some values of this function. Using the result of Problem 10.19, show that the number of molecules of an ideal gas having an X -component of velocity between 0 and v_x is

$$N(0, v_x) = N \text{erf}(x),$$

where $x = (m/2kT)^{1/2} v_x$, and the number of molecules having an X -component of velocity larger than v_x is

$$N(v_x, \infty) = N[\frac{1}{2} - \text{erf}(x)].$$

10.22 What fraction of the molecules of an ideal gas have positive X -components of velocity greater than $2v_{\text{mp}}$?

TABLE 10-1 Values of $\text{erf}(x)$ *

x	$\text{erf}(x)$	x	$\text{erf}(x)$
0	0	1.6	0.4882
0.2	0.1113	1.8	0.4946
0.4	0.2142	2.0	0.4977
0.6	0.3019	2.2	0.4991
0.8	0.3711	2.4	0.4996
1.0	0.4214	2.6	0.4999
1.2	0.4552	2.8	0.5000
1.4	0.4762	3.0	0.5000

* For larger values of x , the values of $\text{erf}(x)$ remain constant at 0.5000, up to four significant figures.

10.23 Compute the fraction of molecules of an ideal gas that have a velocity with a component along the X -axis (a) smaller than v_{mp} , (b) larger than v_{mp} , (c) smaller than v_{ave} , (d) larger than v_{ave} . [Hint: See Problem 10.21.]

10.24 What fraction of the molecules of an ideal gas have X -components of velocity between $-v_{\text{mp}}$ and $+v_{\text{mp}}$?

10.25 Show that the number of molecules of an ideal gas that have a velocity between zero and v is given by

$$N(0, v) = 2N \left[\text{erf}(x) - \frac{1}{\sqrt{\pi}} x e^{-x^2} \right],$$

where $x^2 = mv^2/2kT$. Also find the number of molecules that have a velocity larger than v . [Hint: Use Eq. (10.45) and integrate by parts.]

10.26 Using the result of Problem 10.25, compute the fraction of molecules of an ideal gas that have a velocity (a) smaller than v_{mp} , (b) larger than v_{mp} , (c) smaller than v_{ave} , (d) larger than v_{ave} .

10.27 What percentage of oxygen molecules have velocities greater than 10^3 m s $^{-1}$ at a temperature of (a) 100°K, (b) 1,000°K, (c) 10,000°K? Illustrate graphically in terms of the distribution function.

10.28 Using the result of Problem 10.25, find the percentage of molecules of an ideal gas that have an energy larger than 0.5 eV, given that the temperature is (a) 300°K, (b) 600°K, (c) 1,000°K. [Hint: Note that in the expression derived in Problem 10.25, $x = (E/kT)^{1/2}$.]

10.29 Show that the number of gas molecules with velocity between v and $v + dv$ colliding with the wall of a container, per unit area and per unit time, is $\frac{1}{4}v(dn/dv) dv$. Then show that the total number of molecules colliding with the wall per unit time is $\frac{1}{4}nv_{\text{ave}}$, where n in both cases refers to the number of molecules per unit volume. Note that the molecules with velocity v colliding per unit area and per unit time and moving in a direction making an angle θ with the normal to the wall are those within a cylindrical volume of height equal to $v \cos \theta$. Also the fraction of molecules moving within the solid angle $d\Omega$ is

$$\frac{1}{4\pi} \frac{dn}{dv} dv d\Omega \quad \text{and} \quad d\Omega = 2\pi \sin \theta d\theta.$$

10.30 Assume that a small hole is made in the wall of an oven containing a gas at temperature T . Show that the number of molecules with velocity between v and $v + dv$ escaping per unit area and per unit time is

$$dn = \pi N \left(\frac{m}{2\pi kT} \right)^{3/2} v^3 e^{-mv^2/2kT} dv,$$

where N gives the total number of molecules per unit volume in the oven. Find the total number of molecules escaping per unit area and per unit time. Also show that the average and root-mean-square molecular velocities in the outgoing beam are

$$v_{\text{ave}} = \frac{3}{8} \sqrt{\frac{2\pi kT}{m}}$$

and

$$v_{\text{rms}} = \sqrt{4kT/m}.$$

ALONSO 12+13

12

THERMAL PROPERTIES OF GASES

12.1 Introduction

12.2 The Equation of State of an Ideal Gas

12.3 Equation of State for Real Gases

12.4 Heat Capacity of an Ideal Monatomic Gas

12.5 Heat Capacities of an Ideal Polyatomic Gas

12.6 The Principle of Equipartition of Energy

12.1 Introduction

In the two preceding chapters we have laid the groundwork for a discussion of the general properties of matter in bulk: the mechanical, electrical, thermal, and chemical properties of matter or large aggregates of atoms or molecules. We can approach the discussion of these properties from two opposite directions. The *experimental approach* calls for extensive laboratory measurement and tabulation of properties such as density, specific heat, thermal and electrical conductivities, viscosity, elastic moduli, surface tension, thermal expansion, chemical reaction rates, etc., and the empirical dependence of these quantities on external factors such as pressure and temperature, applied electric and magnetic fields, etc. This has been the traditional procedure for those interested primarily in a knowledge of these properties for specific applications. The alternative approach is *theoretical*; this approach consists in an evaluation of the bulk properties of matter in terms of the atomic and molecular structure and in terms of the interactions between atoms and molecules. Although these interactions are essentially electromagnetic, some simplifying assumptions of a largely phenomenological nature are made (such as a reasonable intermolecular potential energy). Because of the large number of particles involved, the theoretical approach requires the use of statistical methods.

In this chapter we shall illustrate the theoretical procedure by working out some representative problems related to the thermal properties of gases. The extension of the methods of this chapter to other states of matter or to special topics belongs to engineering, physical chemistry, and applied physics, and will not be discussed in this text.

12.2 The Equation of State of an Ideal Gas

The simplest of all systems of particles is an ideal gas, and in this section we shall obtain its equation of state. In Example 11.6 we derived Eq. (11.39), that is,

$$kN \frac{dZ}{Z} = \frac{dW}{T} + \frac{U}{T^2} dT. \quad \left(\frac{dQ}{dT} = 0 \right) \quad (12.1)$$

This equation relates the change in the partition function to the work done by a system and its change in temperature. For the case of a gas, in which the only work is expansion work, we have $dW = p dV$. Also $d(\ln Z) = dZ/Z$. Thus we may rewrite Eq. (12.1) in the form

$$kN d(\ln Z) = \frac{p dV}{T} + \frac{U dT}{T^2}.$$

If the temperature is constant, $dT = 0$, and solving for p , we have

$$p = kNT \left[\frac{\partial(\ln Z)}{\partial V} \right]_T, \quad (12.2)$$

where the subscript T indicates that the temperature is constant. Equation (12.2) relates the pressure of a system to its temperature T , its volume V , and the internal structure of the system, as expressed by Z . Therefore it provides a relation of the form $f(p, V, T) = 0$. Hence we may call Eq. (12.2) the *equation of state of the system*.

For an ideal gas, the partition function is given by Eq. (10.40),

$$Z = \frac{V(2\pi mkT)^{3/2}}{h^3}, \quad (12.3)$$

which, when substituted in Eq. (12.2), gives

$$p = \frac{kNT}{V}. \quad (12.4)$$

Equation (12.4) is the *equation of state of an ideal gas*. It is sometimes written as

$$pV = kNT, \quad (12.5)$$

or, since $R = kN_A = kN/N$, where $N = N/N_A$ is the number of moles of the gas and N_A is Avogadro's number,

$$pV = nRT. \quad (12.6)$$

We can derive this equation in other, perhaps more direct, ways. In one case, we can compute the pressure of the gas by analyzing the change in momentum of the gas molecules when they hit the walls of the container. In another method, we can use the virial theorem to show that Eq. (12.5) gives the pressure of a gas when the intermolecular forces are neglected.* The fact that we arrive at the same result in all derivations shows the consistency of our methods.

** monatomic*

Note on the measurement of temperature. In Section 10.4 we associated the temperature of a system of particles with the average energy of a particle. In Eq. (10.41), which is $E_{k, \text{ave}} = \frac{3}{2}kT$, we were more specific about the relation between the temperature of an ideal gas and the average kinetic energy of the gas molecules. However, we must now consider two important aspects: First, in the defining equation (10.23), we introduced two new quantities, T (the absolute temperature) and k (Boltzmann's constant), and we must decide how they can be measured independently. Second, all human beings have an intuitive concept of temperature based on sensorial experience, as reflected by our feelings of hot and cold. We are all accustomed to measuring temperature in terms of a number given by a device called a *thermometer*. Therefore we must correlate our statistical definition of temperature with this intuitive notion.

Let us consider a mass M of a gas containing N molecules. If we neglect the effect of the intermolecular forces, the equation of state is given by Eq. (12.5); that is, $pV = kNT$.

*See, for example, *Fundamental University Physics*, Volume I, Section 9.13 and Example 9.16.

Suppose that we bring the gas into thermal equilibrium with some other physical system, which we assume may be kept at a fixed temperature. This system may be an equilibrium mixture of water and ice at the standard pressure of 1 atm. This is called the normal freezing point of water. We measure the pressure and the volume of the gas at this fixed temperature, and obtain the values p_0 and V_0 , respectively. Next we decide to assign a convenient (but arbitrary) value T_0 to the fixed temperature, which is also the temperature of the gas. Therefore we may write $p_0 V_0 = kNT_0$. This automatically fixes the value of the Boltzmann constant, $k = p_0 V_0 / NT_0$, since we can obtain N if we know the mass of each molecule.

To determine the temperature of the gas when its pressure is p and its volume is V , so that $pV = kNT$, we simply eliminate the factor kN , using the standard values, and obtain

$$T = T_0(pV/p_0V_0),$$

which gives T in terms of our standard reference temperature T_0 and other measurable quantities. In this way our mass of gas has become a *gas thermometer*. If the volume of the gas is maintained constant and equal to V_0 , we have $T = T_0(p/p_0)$, resulting in a *constant-volume gas thermometer*. We may use other substances as thermometers instead of gases, such as liquids or metals whose dimensions (volume or length) change with the temperature. Other thermometers use electric conductors (such as platinum wires) whose resistance varies with the temperature. Since the equation of state of these substances is more complicated, in practice we calibrate these thermometers against a gas thermometer. In this case the thermometer agrees with the gas thermometer only at the calibration points. Since the property chosen may not vary linearly with the gas temperature, there may be slight discrepancies at intermediate temperatures.

We may choose the value of T_0 on the basis of several points of view. For example, we may choose another process which conceivably occurs at a fixed temperature, such as water boiling at the standard pressure of 1 atm, which is called the normal boiling point of water. Then we may decide that the temperature of this second reference point is 100 units, or *degrees*, above T_0 , chosen as the normal freezing point of water. Given that p_1 and V_1 are the pressure and volume of the gas at this new temperature, we have that $p_1 V_1 = kN(T_0 + 100)$. Solving for kN from the equation $p_0 V_0 = kNT_0$ and substituting this value in the above equation, we find that

$$T_0 = 100p_0V_0/(p_1V_1 - p_0V_0),$$

from which we can obtain a numerical value for T_0 in this arbitrarily chosen scale. The value obtained for T_0 as a result of this type of experiment (and many other experiments using different techniques) is $T_0 = 273.15$. Each of the units is called a *degree Kelvin*, designated by °K. Nowadays it is preferred to simply assign, by definition, the value $T_0 = 273.15$ °K to the temperature of the normal freezing point of water. The value of the Boltzmann constant then becomes $k = 1.3805 \times 10^{-23} \text{ J } ^\circ\text{K}^{-1}$.

It is important to realize that the technique we have explained for measuring temperature is based on the ideal gas approximation. If we use different gases, the results obtained will not be the same because the effect of the intermolecular forces, as it appears in Eq. (12.7) of the next section, is different for each gas. Usually hydrogen or helium is used. It is most desirable to have a temperature scale independent of the substance being used as a measuring medium. We can accomplish this by using a reversible thermal engine operating in a Carnot cycle (see Example 11.7). Then the efficiency of the engine

is independent of the substance used in the engine, and is given by Eq. (11.47), $E = (T_1 - T_2)/T_1$. Given that T_2 is our standard temperature T_0 and T_1 is the temperature T to be measured, we have

$$E = \frac{T - T_0}{T}.$$

Hence if we measure E , we obtain T . It has been found experimentally that for a thermal engine operating between the normal boiling and freezing points of water, $E = 100/373$. If we choose $T - T_0 = 100$ degrees for those two temperatures, we again have that $T_0 = 273^\circ\text{K}$. The temperature obtained using a reversible engine is called the *thermodynamic temperature*. This method was proposed by Kelvin. Both Kelvin and Joule made careful experiments comparing the temperature measured by a constant-volume hydrogen thermometer with the thermodynamic temperature.

12.3 Equation of State for Real Gases

When we are dealing with real gases, we must take into account the intermolecular forces and the finite dimension of the molecules. The intermolecular forces are of fairly short range and decrease rapidly with the distance between molecules. Therefore the pressure of a real gas will be closer to the ideal gas value, Eq. (12.4), the larger the volume per molecule; i.e., the larger V/N . This suggests that we express the pressure of a real gas in terms of the series

$$p = \frac{NRT}{V} + \frac{N^2A}{V^2} + \frac{N^3B}{V^3} + \frac{N^4C}{V^4} + \dots \quad (12.7)$$

in negative powers of V/N . We can consider Eq. (12.7) as *the equation of state of a real gas*. A, B, C, \dots are quantities characteristic of each gas, called the second, third, etc., *virial coefficients*. They are functions of the temperature, and depend on the strength of the intermolecular forces. By measuring p at different temperatures and volumes, we can obtain the virial coefficients $A(T), B(T), \dots$ experimentally. However, to find a clue to the correlation between the virial coefficients and the intermolecular forces, we must obtain certain theoretical relations. One possibility is to use the *virial theorem*, which is derived in mechanics texts.* This theorem, when applied to a gas, becomes

$$pV = NRT + \frac{1}{3} \left(\sum_{\text{All pairs}} F_{ij} \cdot r_{ij} \right)_{\text{ave}}, \quad (12.8)$$

where F_{ij} is the force on molecule i due to molecule j , r_{ij} is the position vector of molecule i relative to molecule j , and the summation extends over all pairs of molecules. When we compare Eq. (12.8) with Eq. (12.7), we find that

$$\frac{1}{3} \left(\sum_{\text{All pairs}} F_{ij} \cdot r_{ij} \right)_{\text{ave}} = N \left(\frac{NA}{V} + \frac{N^2B}{V^2} + \frac{N^3C}{V^3} + \dots \right), \quad (12.9)$$

*See, for example, *Fundamental University Physics*, Volume I, Section 9.12.

which in principle allows us to correlate the virial coefficients A, B, C, \dots with the intermolecular forces. The methods of statistical mechanics allow a more straightforward calculation of the virial coefficients, as we shall presently see. However, because the statistical mechanics of systems composed of interacting particles is slightly more complex than that of systems of noninteracting particles, we shall have to omit some derivations.

Let us introduce the quantity $Z = Z^N/N!$, called the *grand partition function* of a system of noninteracting particles. Then, noting that

$$\ln Z = \ln (Z^N/N!) = N \ln Z - \ln N!,$$

we may also write the equation of state (12.2) in the form

$$p = kT \left[\frac{\partial}{\partial V} (\ln Z) \right]_T. \quad (12.10)$$

For an ideal gas, using Eq. (12.3), we have

$$Z_{\text{ideal}} = \frac{1}{N!} \left[\frac{V(2\pi mkT)^{3/2}}{h^3} \right]^N. \quad (12.11)$$

When we are considering real gases and therefore dealing with interacting molecules, we have to extend the methods of statistical mechanics explained in Chapter 10 to include the internal potential energy $E_p = \sum_{\text{All pairs}} E_{pij}$. We cannot go into the mathematical details of this extension; it is sufficient to indicate that, in the case of a real gas, the grand partition function Z has the form

$$Z = \frac{1}{N!} \left[\frac{(2\pi mkT)^{3/2}}{h^3} \right]^N \iint \dots \int_{\text{All molecules}} e^{-E_p/kT} dV_1 dV_2 \dots dV_N, \quad (12.12)$$

where the N volume integrals correspond to one for each molecule. This apparently formidable expression is, in fact, a very simple extension of the partition function for an ideal gas, because for an ideal gas we must make $E_p = 0$ and then $e^{-E_p/kT} = 1$. Thus the multiple integral becomes

$$\iint \dots \int_{\text{All molecules}} dV_1 dV_2 \dots dV_N = V \cdot V \cdot V \dots = V^N, \quad (12.13)$$

since each molecule may be found throughout the entire available volume. Then Eq. (12.12) becomes

$$Z_{\text{ideal}} = \frac{1}{N!} \left[\frac{(2\pi mkT)^{3/2}}{h^3} \right]^N V^N = \frac{1}{N!} \left[\frac{V(2\pi mkT)^{3/2}}{h^3} \right]^N,$$

in agreement with Eq. (12.11).

Now, returning to Eq. (12.12), we must write the potential energy as

$$E_p = \sum_{\text{All pairs}} E_{pij}$$

and use a reasonable expression for the intermolecular potential energy. Once we know E_p , we may in principle evaluate Z . By applying Eq. (12.10), we can obtain the pressure p and expand the result in inverse powers of the volume V . In this way we can establish a relation between the intermolecular potential E_{pij} and the virial coefficients A, B, \dots . Since we can determine the virial coefficients A, B, \dots experimentally, this provides a very useful guide for investigating the form of the intermolecular potential E_{pij} on a sort of trial-and-error basis until we can calculate the correct virial coefficients. We shall illustrate some of these techniques in the remainder of this section.

Let us consider the multiple integral of Eq. (12.12); that is,

$$I = \iint \dots \int_{\text{All molecules}} e^{-E_p/kT} dV_1 dV_2 \dots dV_N,$$

where the summation

$$E_p = \sum_{\text{All pairs}} E_{pij}$$

contains $\frac{1}{2}N(N-1)$ terms, which is the total number of different pairs of molecules. Noting that

$$e^{(x+y+z+\dots)} = e^x \cdot e^y \cdot e^z \dots,$$

we have that

$$e^{-E_p/kT} = \prod_{\text{All pairs}} e^{-E_{pij}/kT},$$

where the symbol \prod means the product of all terms appearing. Also when E_{pij} is very small, the exponential factor is practically 1. But (except when the molecules are rather close) E_{pij} is very small, due to the short range of the intermolecular forces (see Fig. 12-1). Thus, using the expansion $e^{-x} = 1 - x + \frac{1}{2}x^2 - \dots$, we can write

$$e^{-E_{pij}/kT} = 1 - \frac{E_{pij}}{kT} + \frac{1}{2} \left(\frac{E_{pij}}{kT} \right)^2 \dots = 1 + f_{ij}, \quad (12.14)$$

and the quantity f_{ij} is very small except when the two molecules are very close. Therefore

$$e^{-E_p/kT} = \prod_{\text{All pairs}} (1 + f_{ij}) = 1 + \sum_{\text{All pairs}} f_{ij} + \dots$$

The terms that have been omitted involve products of 2, 3, ... f_{ij} 's, and we shall neglect them, although, in a more detailed theory, they must be considered. With

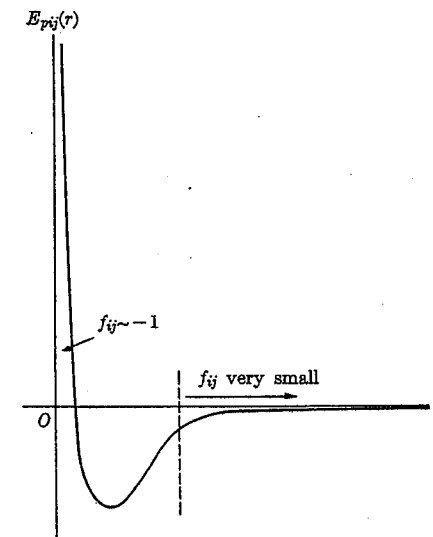


Fig. 12-1. Intermolecular potential energy.

this approximation we may write the integral I as

$$I = \int \cdots \int \left(1 + \sum_{\substack{\text{All} \\ \text{molecules}}} f_{ij} + \cdots \right) dV_1 dV_2 \cdots dV_N.$$

The term having the factor 1 obviously gives V^N after integration, in agreement with the previous result for an ideal gas in Eq. (12.13). Succeeding terms then give the contribution of the intermolecular forces. The $\frac{1}{2}N(N-1)$ terms of the summation are all alike, because f_{ij} has the same form for all pairs of molecules. Thus we may write their contribution in the form

$$\frac{1}{2}N(N-1)V^{N-2} \int_1 \int_2 f_{12} dV_1 dV_2, \quad (12.15)$$

where we have chosen the pair of molecules 1 and 2 and the factor V^{N-2} results from the volume integral for the remaining $N-2$ molecules. In evaluating the double integral, we may first choose our origin of coordinates at molecule 1 to perform the integral over dV_2 (Fig. 12-2). Designating the distance between 1 and 2 by r , we may then write

$$\begin{aligned} \int_1 \int_2 f_{12}(r) dV_1 dV_2 \\ = \int_1 \left\{ \int_2 f_{12}(r) 4\pi r^2 dr \right\} dV_1 \end{aligned}$$

where we have used $dV_2 = 4\pi r^2 dr$ for the volume element, because of the spherical symmetry of the problem. The integral

$$\beta = \int_0^\infty f_{12}(r) 4\pi r^2 dr \quad (12.16)$$

is independent of the position of molecule 1 (so long as it is not close to the walls of the container), and therefore

$$\int_1 \int_2 f_{12}(r) dV_1 dV_2 = \int_1 \beta dV_1 = \beta \int dV_1 = \beta V.$$

Replacing $\frac{1}{2}N(N-1)$ by $\frac{1}{2}N^2$, which is a valid approximation when N is very large, we then have Eq. (12.15) in the form $\frac{1}{2}N^2 V^{N-1} \beta$, and we may write the integral I as

$$I = V^N + \frac{1}{2}N^2 V^{N-1} \beta = V^N \left(1 + \frac{N\beta}{2V} \right).$$

However, if successive terms are taken into account in the expansion of $e^{-E_p/kT}$, the result one obtains for I is

$$I = V^N \left(1 + \frac{N\beta}{2V} \right)^N.$$

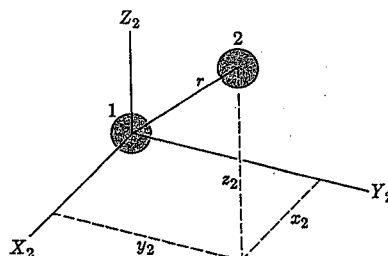


Figure 12-2

The previous result is just the first two terms in the binomial expansion of the above expression. The grand partition function of the real gas, Eq. (12.12), is now given by the expression

$$Z = \frac{1}{N!} \left[\frac{V(2\pi mkT)^{3/2}}{h^3} \right]^N \left(1 + \frac{N\beta}{2V} \right)^N \quad (12.17)$$

up to the first order of approximation. This must be compared with Eq. (12.11) for a real gas. The last factor in Eq. (12.17) is the contribution of the intermolecular forces to the grand partition function.

To obtain the equation of state of a real gas, we now use Eq. (12.10). From the expression (12.17) for Z , we have

$$\ln Z = N \ln V + N \ln \left(1 + \frac{N\beta}{2V} \right) + F(T),$$

where we have included in $F(T)$ the remaining terms that are either constant or depend on the temperature and do not affect the derivative in Eq. (12.10). We now approximate the second term, using $\ln(1+x) \sim x$ under the assumption that $x (=N\beta/2V)$ is small compared with 1 (the quantity $N\beta/2V$ is of the order of 10^{-4} at STP). Thus

$$\ln Z = N \ln V + \frac{N^2 \beta}{2V} + F(T).$$

Therefore

$$\left[\frac{\partial}{\partial V} (\ln Z) \right]_T = \frac{N}{V} - \frac{N^2 \beta}{2V^2}$$

which, substituted in Eq. (12.10), gives

$$p = kT \left[\frac{N}{V} - \frac{N^2 \beta}{2V^2} \right] = \frac{kNT}{V} - \frac{kTN^2 \beta}{2V^2}.$$

But remembering that $N = nN_A$ and $R = kN_A$, we may write

$$p = \frac{nRT}{V} - \frac{n^2 RT N_A \beta}{2V^2}, \quad (12.18)$$

which is the resulting equation of state of the real gas expressed in virial form, to the first order of approximation. We note that in Eq. (12.18) we have obtained only two terms; this is a result of the type of the approximation which we have made in the evaluation of Z . When we take these terms into account, the complete virial expansion results. Comparing Eq. (12.18) with Eq. (12.7), we see that the second virial coefficient in our approximation is

$$A(T) = -\frac{1}{2}RT N_A \beta, \quad (12.19)$$

which directly relates the intermolecular interaction (identified by β) and the virial coefficient $A(T)$ (determined experimentally). This is the connection between the intermolecular interaction and the virial coefficients that we indicated before.

We shall not pursue our discussion any further; what we have said is enough to indicate the method of attacking the problem of the equation of state of a real gas, and in general of any system composed of interacting molecules. The case for liquids and solids is more complex, and we shall not discuss it in this text.

EXAMPLE 12.1. Evaluate the second virial coefficient for the case of a gas composed of noninteracting hard spheres of radius r_0 .

Solution: This is a rather "unrealistic" real gas because no intermolecular forces are assumed until the centers of the molecules are a distance $2r_0$ apart, at which time a strong repulsion sets in. Thus the intermolecular potential energy is $E_{p12} = 0$ for $r > 2r_0$ and $E_{p12} = \infty$ for $r < 2r_0$, resulting in $f_{12} = 0$ for $r > 2r_0$ and $f_{12} = -1$ for $r < 2r_0$. This "hard-core" potential, as it is usually called, is represented in Fig. 12-3. We have called this an unrealistic potential energy because it cannot produce condensation, since it has no minimum and therefore no stable separation between the molecules. However, it does give us a simple model with which to check our physical ideas without undue mathematical complications. Introducing the values of f_{12} in Eq. (12.16), we obtain

$$\beta = \int_0^{2r_0} (-1)4\pi r^2 dr = -\frac{4}{3}\pi(2r_0)^3 = -\frac{32\pi r_0^3}{3}.$$

When we substitute this value in Eq. (12.19), the second virial coefficient becomes

$$A = RTN_A \left(\frac{16\pi r_0^3}{3} \right) = RTb,$$

where $b = N_A(16\pi r_0^3/3)$ is four times the volume of the molecules in one mole. Hence the equation of state of a gas composed of hard spheres, to the first-order approximation, is

$$p = \frac{NRT}{V} + \frac{N^2 RTb}{V^2}.$$

EXAMPLE 12.2. Extend the results of the previous example to the case in which the intermolecular forces are attractive but very weak, except for $r < 2r_0$, where a very strong repulsion sets in, making the molecules almost like impenetrable hard spheres.

Solution: As a logical extension of the calculation performed in the previous example, we may introduce rather weak but attractive intermolecular forces for $r > 2r_0$, as illustrated in Fig. 12-4. Then we may continue with the assumption that $f_{ij} = -1$ for $r < 2r_0$. But from Eq. (12.14), if E_{p12}/kT is small compared with unity, we may write $f_{12} = -E_{p12}/kT$ for $r > 2r_0$. Therefore Eq. (12.16) gives

$$\beta = \int_0^{2r_0} (-1)4\pi r^2 dr + \int_{2r_0}^{\infty} (-E_{p12}/kT)4\pi r^2 dr = -\frac{32\pi r_0^3}{3} + \frac{\alpha}{kT},$$

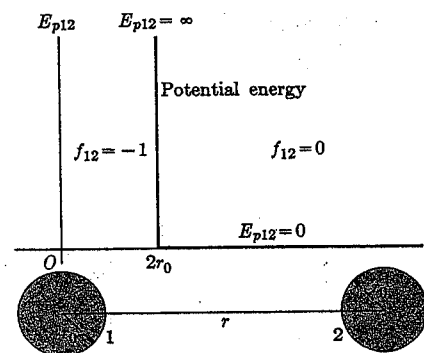


Fig. 12-3. Hard-core intermolecular potential energy. No attraction at any distance.

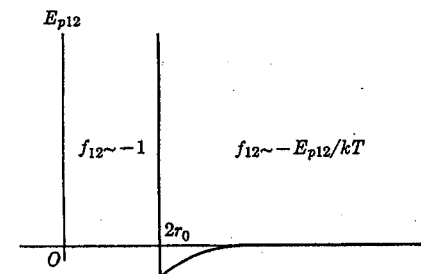


Fig. 12-4. Intermolecular potential energy with a hard core and weakly attractive at larger distances.

where

$$\alpha = \int_{2r_0}^{\infty} (-E_{p12})4\pi r^2 dr$$

is a positive quantity, since E_{p12} is negative (see Fig. 12-4) for $r > 2r_0$. Substituting in Eq. (12.19), using our previous definition of b and setting $a = \frac{1}{2}N_A^2\alpha$, we obtain $A = RTb - a$ for the second virial coefficient. The equation of state, to the first order of approximation, is then, using Eq. (12.7),

$$p = \frac{NRT}{V} + \frac{N^2(RTb - a)}{V^2} + \dots \quad (12.20)$$

This equation is satisfied with fairly good accuracy by many real gases, especially for large values of V/N . The coefficients a and b are called *van der Waals constants*. They are given in Table 12-1 for several real gases.

TABLE 12-1 Van der Waals Constants

Substance	a , $\text{N m}^4 \text{ kg}^{-2} \text{ mole}^{-2}$	b , $\text{m}^3 \text{ kg}^{-1} \text{ mole}^{-1}$
Helium	3.446×10^3	0.02370
Hydrogen	24.68	0.02661
Neon	21.28	0.01709
Nitrogen	140.4	0.03913
Oxygen	137.4	0.03183
Ammonia	421.2	0.03707
Carbon dioxide	362.8	0.04267
Sulfur dioxide	678.1	0.05636
Water	551.9 / 55.2	0.03049 / 55.5

12.4 Heat Capacity of an Ideal Monatomic Gas

In Section 11.7 we defined the heat capacities of a substance at constant volume and at constant pressure as

$$C_V = \frac{1}{N} \left(\frac{\partial U}{\partial T} \right)_V, \quad C_p = \frac{1}{N} \left(\frac{\partial H}{\partial T} \right)_p, \quad (12.21)$$

where $H = U + pV$ is the enthalpy of the substance. In addition to their importance as coefficients in several practical calculations, the theoretical calculation of the heat capacities of a substance affords a means of verifying the correctness of the model chosen to describe the substance. In this section we shall calculate the heat capacities of an ideal gas, and by comparing these with the observed values for real gases, we shall be able to conclude to what extent the ideal-gas model is a good approximation.

Let us first consider an ideal monatomic gas. The internal energy of such a gas is purely translational kinetic energy, and is given by $U = \frac{3}{2}NRT$. Using Eq. (12.21), we obtain

$$C_V = \frac{3}{2}R = 12.4715 \text{ J mole}^{-1} \text{ } ^\circ\text{K}^{-1} \\ = 2.9807 \text{ cal mole}^{-1} \text{ } ^\circ\text{C}^{-1}. \quad (12.22)$$

Taking into account Eq. (12.6) ($pV = NRT$), we have that the enthalpy of an ideal gas is

$$H = U + pV = \frac{5}{2}NRT.$$

Thus Eq. (12.21) gives

$$C_p = \frac{5}{2}R = 20.7858 \text{ J mole}^{-1} \text{ } ^\circ\text{K}^{-1} \\ = 4.9678 \text{ cal mole}^{-1} \text{ } ^\circ\text{C}^{-1}. \quad (12.23)$$

Therefore all ideal monatomic gases have the same heat capacities, independent of the structure of the atoms. We may note, from the above results, that

$$C_p - C_V = R, \quad (12.24)$$

so that C_p is larger than C_V by the amount R . The reason for this is that C_V is related only to the change in internal energy, while C_p includes, in addition, the expansion work of the gas when its temperature increases 1 degree at constant pressure. It is simple to verify that this work is exactly equal to R . When the pressure of the gas is constant, $p dV = nR dT$, and if the increase of temperature is one degree, the work done is

$$W_p = \int p dV = \int_T^{T+1} nR dT = nR.$$

Hence the work per mole done by the gas is R . From this proof we see that Eq. (12.24) is valid for all ideal gases, either monatomic or otherwise.

Another relation among the heat capacities of an ideal monatomic gas is

$$\gamma = C_p/C_V = \frac{5}{3} = 1.667. \quad (12.25)$$

This relation is followed rather closely by most monatomic gases, as shown in Table 12-3 (at the end of this chapter).

EXAMPLE 12.3. The equation of state of an ideal gas in terms of pressure, volume, and entropy.

Solution: Since entropy is a property of the state of a gas, it can be used as a variable to define the state of a gas in the same way as pressure, volume, or temperature. From the equation of state, $pV = nRT$, we have

$$\ln p + \ln V = \ln nR + \ln T.$$

Differentiation yields

$$\frac{dp}{p} + \frac{dV}{V} = \frac{dT}{T}. \quad (12.26)$$

For the case of an ideal gas, in which the internal energy depends solely on the temperature, we have that $dU = nC_V dT$. Therefore the first law of thermodynamics, Eq. (11.37), $dU = T dS - p dV$, gives

$$nC_V dT = T dS - p dV,$$

from which (dividing by T and using the equation of state) we obtain

$$nC_V \frac{dT}{T} = dS - nR \frac{dV}{V}. \quad (12.27)$$

Eliminating dT/T between Eqs. (12.26) and (12.27) and using the relation $C_p - C_V = R$, we have

$$\frac{dp}{p} + \gamma \frac{dV}{V} = \frac{dS}{nC_V},$$

where $\gamma = C_p/C_V$. Integrating, we obtain

$$\ln p + \gamma \ln V = \frac{S}{nC_V} + \ln (\text{const})$$

or

$$pV^\gamma = (\text{const})e^{S/nC_V}, \quad (12.28)$$

which is the equation of state of an ideal gas in terms of p , V , and S . If a transformation is adiabatic and reversible (i.e., if it is isentropic), the equation reduces to

$$pV^\gamma = \text{const}. \quad (12.29)$$

This equation finds many uses in processes involving gases.

12.5 Heat Capacities of an Ideal Polyatomic Gas

When the ideal gas is not monatomic, we must take the structure of the molecules into account when we calculate the heat capacities. The energy of a polyatomic molecule is composed of three terms: translational energy, rotational energy, and vibrational energy; that is,*

$$E_{\text{molecule}} = E_{\text{tr}} + E_{\text{rot}} + E_{\text{vib}}. \quad (12.30)$$

We shall ignore the electronic energy of the molecules because it seldom participates in the thermal excitation of the gas. Electronic excitation requires an energy of the order of 1 eV at least; such energy is about 40 times greater than the average thermal kinetic energy at room temperature (298°K), and therefore a temperature of the order of 10^4 °K is required to produce a substantial number of molecules in excited electronic states (see Example 10.4). At these temperatures, of course, most of the gas molecules are dissociated by collisions.

On the other hand, the rotational kinetic energy of polyatomic molecules is of the order 10^{-4} eV, and therefore molecules can easily be carried to excited rotational levels, even at temperatures that are low compared with room temperature. Vibrational energies are in the range of 10^{-3} eV to 10^{-1} eV, and therefore at room temperature molecules may be found in a few low-lying excited vibrational states.

To compute the contribution of the internal motions to the heat capacity of a polyatomic gas, we must first (using statistical methods) find the distribution of the gas molecules among the rotational and vibrational states. Let us limit ourselves to the simplest case of a diatomic gas. The rotational kinetic energy of diatomic molecules, according to Eq. (5.12), is

also: diatomic
$$E_{\text{rot}} = \frac{\hbar^2 l(l+1)}{2I}, = \frac{L^2}{2I} \quad I = \mu r_0^2$$

where I is the moment of inertia of the molecule relative to a perpendicular axis passing through the center of mass and l determines the angular momentum of the molecule relative to the center of mass. As explained in Section 5.7, the angular momentum may have $2l + 1$ different orientations, all with the same energy, so that the g_l factor used in Eq. (10.23) is $2l + 1$. The equilibrium distribution of the molecules among the available rotational states, when we use Maxwell-Boltzmann statistics, is then

$$n_{\text{rot}} = \frac{N}{Z_{\text{rot}}} (2l + 1) e^{-\hbar^2 l(l+1)/2IkT} = \frac{N}{Z_{\text{rot}}} (2l + 1) e^{-l(l+1)\Theta_r/T}, \quad (12.31)$$

where $\Theta_r = \hbar^2/2Ik$ is called the *characteristic temperature of rotation*. Values of Θ_r are given in Table 12-2 for a few diatomic gases. Looking at this table, we can

*We shall assume, for simplicity, that the three energies are additive. However, strictly speaking, there are some cross terms among the rotational and vibrational energies.

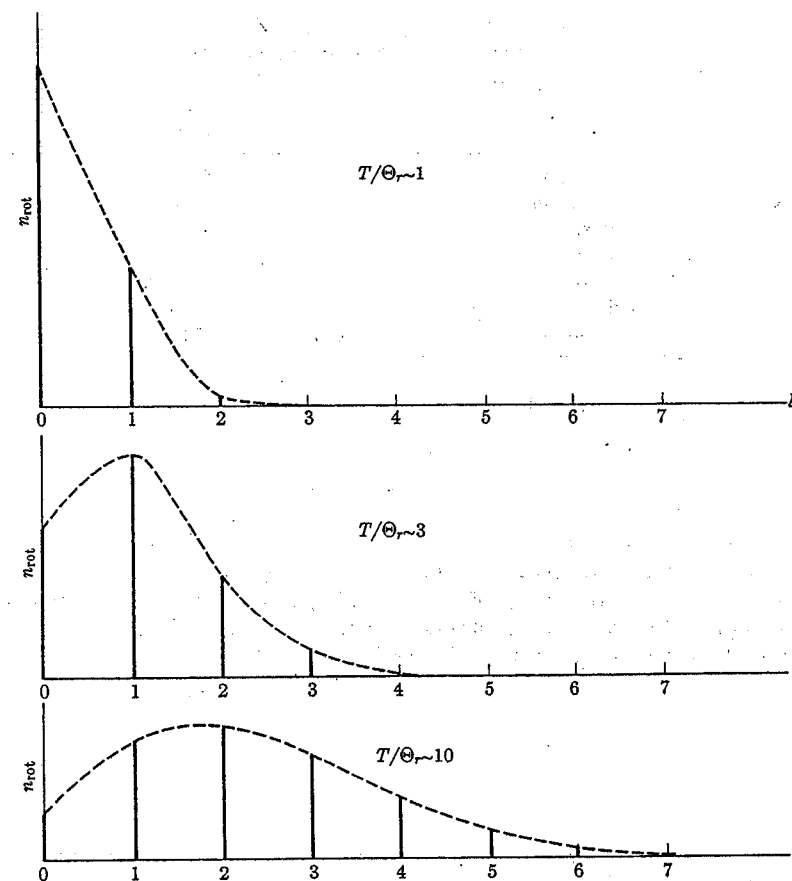


Fig. 12-5. Occupation of rotational levels in a diatomic gas for three values of T/Θ_r .

see that even for hydrogen these values are very small compared with room temperature. The values of n_{rot} are illustrated in Fig. 12-5 for three values of T/Θ_r . As T increases, the number of molecules in excited rotational states also increases.

The rotational partition function Z_{rot} , according to the general definition in Eq. (10.22), is

$$Z_{\text{rot}} = \sum_l (2l + 1) e^{-l(l+1)\Theta_r/T}. \quad (12.32)$$

Once we compute the rotational partition function Z_{rot} , we can obtain the rotational energy U_{rot} of the gas by using Eq. (10.24):

$$U_{\text{rot}} = kNT^2 \frac{d}{dT} (\ln Z_{\text{rot}}). \quad (12.33)$$

TABLE 12-2 Characteristic Temperatures for Rotation and Vibration of Diatomic Molecules

Substance	Θ_r , °K	Θ_v , °K
Hydrogen	85.5	6140
Carbon monoxide	2.77	3120
Oxygen	2.09	2260
Chlorine	0.347	810
Bromine	0.117	470
Sodium	0.224	230
Potassium	0.081	140

The total internal energy of the gas is

$$U = U_{tr} + U_{rot} = \frac{5}{2}NRT + U_{rot}, \quad (12.34)$$

since $U_{tr} = \frac{3}{2}NRT$. To obtain the heat capacity at constant volume, C_V , we next substitute Eq. (12.34) in Eq. (12.21). The heat capacity increases gradually with the temperature, as indicated in Fig. 12-6, because energy is required not only to increase the translational energy of the molecules, but also to increase their rotational energy by bringing more molecules to excited rotational levels. Figure 12-6 indicates that, at a temperature high relative to Θ_r , C_V levels off at about $\frac{5}{2}R$.

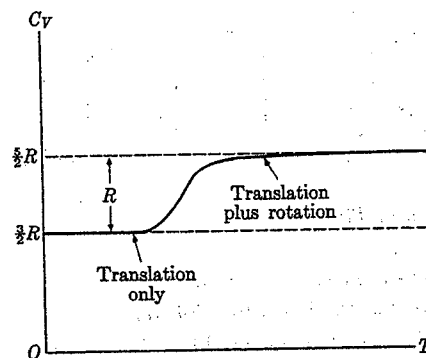


Fig. 12-6. Variation of heat capacity at constant volume of a diatomic gas due to excitation of rotational levels.

We can explain this as follows: At temperatures much higher than Θ_r (so that Θ_r/T is very small), a very large number of rotational states are occupied. Also the spacing of the rotational levels becomes very small compared with the thermal energy, and we may compute Z_{rot} by replacing the summation in Eq. (12.32) by an integration. We also substitute $2l$ for $2l+1$ and l^2 for $l(l+1)$. Then

$$Z_{rot} = \int_0^\infty 2l e^{-(\Theta_r/T)l^2} dl = T/\Theta_r.$$

Thus $\ln Z_{rot} = \ln T - \ln \Theta_r$, and Eq. (12.33) gives

$$U_{rot} = kNT = NRT, \quad (12.35)$$

since $kN = N$. Then the total energy at $T \gg \Theta_r$ is

$$U = U_{tr} + U_{rot} = \frac{5}{2}NRT + NRT = \frac{7}{2}NRT. \quad (12.36)$$

Substituting Eq. (12.36) in Eq. (12.21), we get

$$C_V = \frac{5}{2}R. \quad (12.37)$$

Thus, at temperatures high compared with Θ_r , the rotational kinetic energy of a diatomic molecule contributes an amount R to the heat capacity at constant volume of the ideal diatomic gas. The same result holds true for gases composed of linear polyatomic molecules.

Now let us compute the vibrational energy of the ideal diatomic gas. We assume that the vibrations are simple harmonic; then the vibrational energy levels, according to Eq. (5.16), are given by $E_{vib} = (v + \frac{1}{2})\hbar\omega$. Therefore, when we again use Maxwell-Boltzmann statistics and $g_i = 1$, which corresponds to this case, the occupation of the vibrational levels is

$$n_{vib} = \frac{N}{Z_{vib}} e^{-(v+1/2)\hbar\omega/kT} = \frac{N}{Z_{vib}} e^{-(v+1/2)\Theta_v/T}, \quad (12.38)$$

where $\Theta_v = \hbar\omega/k$ is called the characteristic temperature for vibration. Its value for a few diatomic molecules is given in Table 12-2. Note that in all cases Θ_v is much larger than Θ_r . Also in most cases Θ_v is greater than room temperature. Figure 12-7 shows the values of n_{vib} for three values of T/Θ_v . As T increases, the number of molecules in excited vibrational levels also increases; but because $\Theta_v > \Theta_r$, the excited low vibrational levels begin to be appreciably populated at temperatures at which many rotational levels are already occupied. In some cases the molecules dissociate at energies lower than those at which the higher vibrational levels contribute appreciably to the internal energy.

The vibrational partition function Z_{vib} is

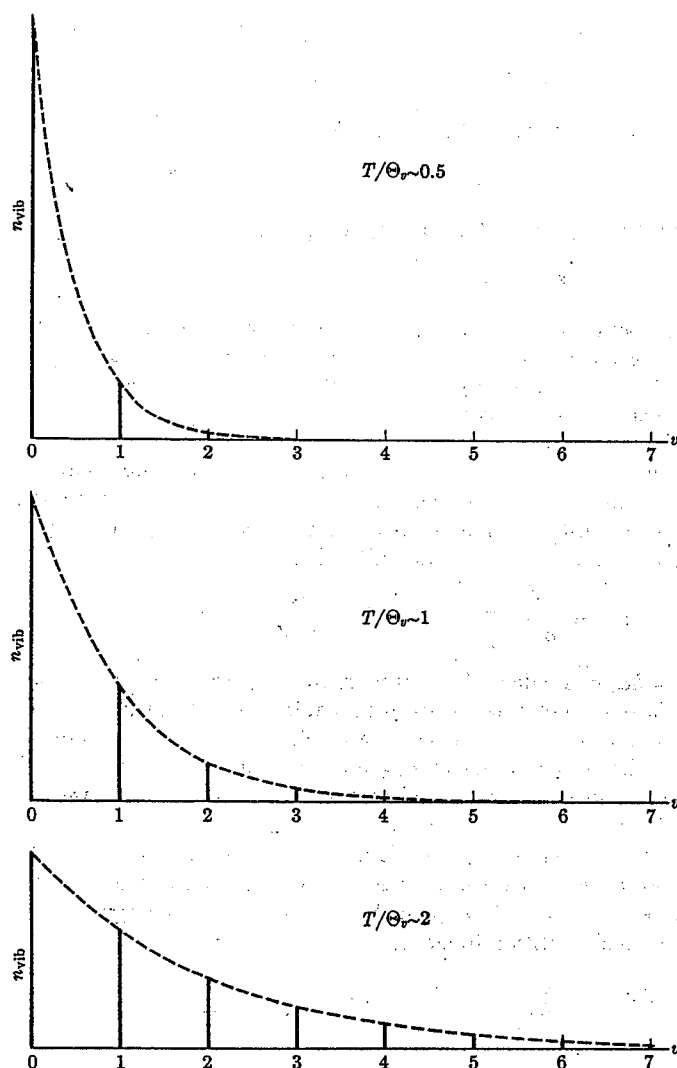
$$Z_{vib} = \sum_v e^{-(v+1/2)\Theta_v/T} = e^{-\Theta_v/2T} \left(\sum_v e^{-v\Theta_v/T} \right). \quad (12.39)$$

Using the expression for the sum of an infinite decreasing geometric progression,

$$\sum x^n = 1 + x + x^2 + x^3 + \cdots = \frac{1}{1-x}, \quad \text{for } x < 1,$$

and noting that in our case $x = e^{-\Theta_v/T}$, we have for the vibrational partition function

$$Z_{vib} = \frac{e^{-\Theta_v/2T}}{1 - e^{-\Theta_v/T}}. \quad (12.40)$$

Fig. 12-7. Occupation of vibrational levels in a diatomic gas for three values of T/Θ_v .

From this result we have

$$\ln Z_{\text{vib}} = -\Theta_v/2T - \ln(1 - e^{-\Theta_v/T})$$

and

$$\frac{d}{dT}(\ln Z_{\text{vib}}) = \frac{\Theta_v}{2T^2} + \frac{\Theta_v/T^2}{e^{\Theta_v/T} - 1}$$

According to Eq. (10.24), the vibrational energy of the gas is obtained by

$$U_{\text{vib}} = kNT^2 \frac{d}{dT}(\ln Z_{\text{vib}}) = \frac{1}{2}kN\Theta_v + \frac{kN\Theta_v}{e^{\Theta_v/T} - 1}. \quad (12.41)$$

Recalling, from Section 5.8, that $\frac{1}{2}k\Theta_v = \frac{1}{2}\hbar\omega$ is the zero-point vibrational energy of a molecule, we recognize that the term $\frac{1}{2}kN\Theta_v$ is the total zero-point vibrational energy of the gas. This constant energy, although it may be rather large, does not affect any process in which only energy differences are involved. To compute the heat capacity at constant volume, we must add U_{vib} to $U_{\text{tr}} + U_{\text{rot}}$, and again apply Eq. (12.21). For large temperatures the quantity Θ_v/T is very small; hence, using the approximation $e^x = 1 + x + \dots$ for small x , we may write

$$e^{\Theta_v/T} - 1 = \left(1 + \frac{\Theta_v}{T} + \dots\right) - 1 = \frac{\Theta_v}{T} + \dots, \quad (12.42)$$

so that Eq. (12.41) becomes

$$U_{\text{vib}} = \frac{1}{2}kN\Theta_v + kNT = kNT(1 + \Theta_v/2T). \quad (12.43)$$

Thus the molecular vibrations contribute to the internal energy by an amount whose value, for temperatures much larger than Θ_v , is

$$U_{\text{vib}} = kNT = NRT. \quad (12.44)$$

This energy happens to be the same as for the rotational energy given by Eq. (12.35). The asymptotic value of the total energy at very high temperatures is

$$U = U_{\text{tr}} + U_{\text{rot}} + U_{\text{vib}} = \frac{3}{2}NRT + NRT + NRT = \frac{7}{2}NRT,$$

corresponding to a total heat capacity

$$C_V = \frac{7}{2}R. \quad (12.45)$$

Comparing this value with Eq. (12.37), we conclude that at high temperatures the vibrations of diatomic molecules contribute an amount R to the specific heat at constant volume of the diatomic gas.

Figure 12-8 shows, for a diatomic gas, the general trend of C_V as the temperature increases. This trend is well confirmed by experimental measurements.

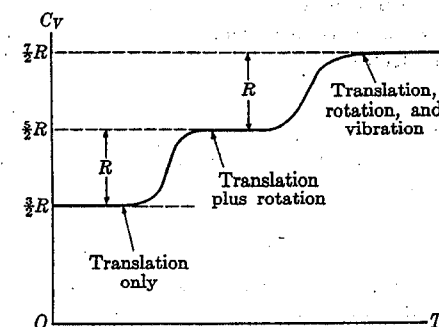


Fig. 12-8. Variation of heat capacity at constant volume of a diatomic gas due to excitation of rotational and vibrational levels.

12.6 The Principle of Equipartition of Energy

The average kinetic energy of the molecules of an ideal gas due to their translational motion is

$$E_{\text{ave}} = \frac{3}{2}kT. \quad (12.46)$$

Now translational motion is associated with the three coordinates x, y, z required to fix the center of mass of the molecule. We may then assume that, in view of the symmetry of space, the average kinetic energy for the motion along each of the coordinate axes is

$$\epsilon = \frac{1}{2}kT. \quad (12.47)$$

Therefore, if a gas were constrained so that its molecules could move only in a plane with two degrees of freedom or coordinates, we would expect that the average kinetic energy of the molecules would be twice ϵ , or kT .

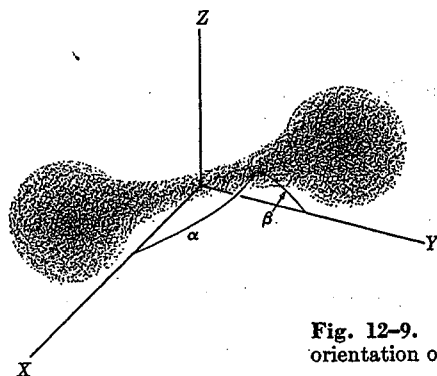


Fig. 12-9. Two angles are required to fix the orientation of a linear molecule in space.

Now let us consider the rotation of a diatomic (or a linear) molecule. The orientation of the axis of the molecule (Fig. 12-9) is determined by the angles α and β it makes with any two coordinate axes, such as X and Y . Then the rotation of a diatomic (and in general of any linear) molecule has two degrees of freedom. We may thus expect, by extension of Eq. (12.47) to the rotational motion of a molecule, that the average kinetic energy of rotation of a molecule is

$$E_{\text{ave}}(\text{rot}) = 2\epsilon = kT,$$

and that the total energy of rotation of a gas composed of diatomic (or linear) molecules would be

$$U_{\text{rot}} = NE_{\text{ave}}(\text{rot}) = kNT = NRT.$$

This agrees with the result given in Eq. (12.35), which is valid for temperatures high compared with Θ_r .

Similarly, the vibrational motion of a diatomic molecule has only one degree of freedom, and the average vibrational energy of such a molecule should be $\epsilon = \frac{1}{2}kT$; however, in vibrational motion we have *both* kinetic and potential energy and their average values are equal. Therefore the average vibrational energy of a molecule is twice the kinetic energy per degree of freedom, or

$$E_{\text{ave}}(\text{vib}) = 2\epsilon = kT,$$

and the total energy of vibration of the diatomic gas would be

$$U_{\text{vib}} = NE_{\text{ave}}(\text{vib}) = kNT = NRT.$$

This again coincides with the result given in Eq. (12.44), which is valid for temperatures high compared with Θ_v .

We may then establish a very important rule, called the *principle of equipartition of energy*:

At temperatures sufficiently high so that kT is large compared with the spacing of the energy levels associated with a certain degree of freedom of the molecules, the average molecular energy per degree of freedom is $\frac{1}{2}kT$. (Vibrational energy contributes an amount of energy kT per vibrational degree of freedom because of the potential energy involved.)

This principle will help us to extend the discussion of the preceding section to polyatomic molecules. Consider a polyatomic molecule which has 3 degrees of freedom for translational motion and f internal degrees of freedom for rotational and vibrational motion (with each vibration counting as two degrees). The average molecular energy at high temperatures of a gas composed of such molecules is given by

$$E_{\text{ave}} = (3 + f)\epsilon = \frac{3 + f}{2}kT,$$

and the total internal energy of the gas is given by

$$U = NE_{\text{ave}} = \frac{3 + f}{2}kNT = \frac{3 + f}{2}NRT.$$

The heat capacity of the gas at constant volume tends, at high temperature, to the value

$$C_V = \frac{3 + f}{2}R. \quad (12.48)$$

Now, according to Eq. (12.24), $C_p - C_V = R$ or $C_p = C_V + R$, which is valid for all ideal gases regardless of their molecular structure. If we use Eq. (12.48) for C_V , we obtain

$$C_p = \frac{5 + f}{2}R. \quad (12.49)$$

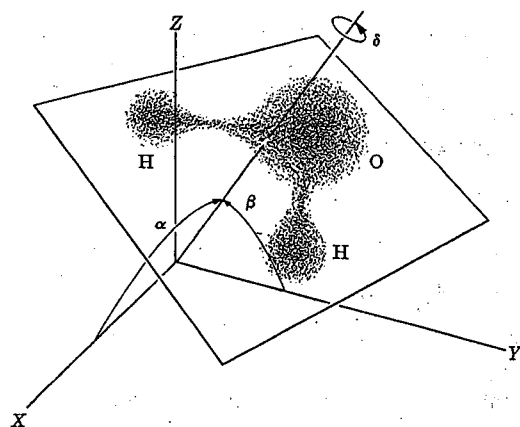


Fig. 12-10. Three angles are needed to fix the orientation of a nonlinear molecule, such as H_2O , in space.

The ratio $\gamma = C_p/C_v$ then has the value

$$\gamma = \frac{C_p}{C_v} = \frac{5+f}{3+f}. \quad (12.50)$$

Actually f in these formulas corresponds only to those degrees of freedom for which a very large number of excited states are occupied at the given temperature. Thus if T is larger than Θ_r but smaller than Θ_v , f corresponds only to the rotational degrees of freedom. But if T is much larger than Θ_v , then f corresponds to all the degrees of freedom. For a monatomic gas $f = 0$ and $\gamma = \frac{5}{3} = 1.67$, as previously indicated in Eq. (12.25). For a diatomic gas (and in general for any linear molecule in the gaseous state), we have, at room temperature (when only rotational motion counts), that $f = 2$ and $\gamma = \frac{7}{5} = 1.40$. If the molecule is not linear but planar, like water (H_2O), or three-dimensional, like ammonia (NH_3), there are three rotational degrees of freedom because, in addition to the angles α and β needed to fix the axis (Fig. 12-10), we need the angle δ of rotation around

TABLE 12-3 Ratios of the Heat Capacities for Some Gases

Substance	γ	f	Substance	γ	f
Helium	1.659	$\frac{5}{3}$	Chlorine	1.355	
Neon	1.64		Hydrogen sulfide	1.32	$\frac{5}{3}$
Argon	1.668		Water vapor	1.324	
Hydrogen	1.410		Ammonia	1.310	
Oxygen	1.401	$\frac{7}{5}$	Carbon dioxide	1.304	
Nitrogen	1.404		Ethylene	1.255	
Carbon monoxide	1.404				

the axis. Thus $f = 3$ and $\gamma = \frac{8}{5} = 1.33$. Therefore the measurement of γ can provide important information about the internal structure of a molecule. For example, from Table 12-3, which gives the value of γ for several gases, we see that H_2O is planar and not linear, and that the inert gases are all monatomic ($f = 0$). The CO_2 molecule is a notable exception because, although it is linear, it has $\gamma = 1.304$, close to the value of a planar molecule. We know that CO_2 is linear because its electric dipole moment is zero. The apparent discrepancy is attributable to the fact that a bending vibrational mode in CO_2 has a relatively small vibrational energy. This vibration adds two degrees of freedom, and thus the ratio of heat capacities for CO_2 should be close to $\frac{7}{5} = 1.285$.

$f=4$

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Problems

P (12.1) Using the virial expansion for the equation of state of a gas as given by Eq. (12.20), calculate the work done by a gas when it expands isothermally from a volume V_1 to a volume V_2 . Apply the result to one mole of hydrogen at 300°K when it expands from a volume of $3 \times 10^{-2} \text{ m}^3$ to a volume of $5 \times 10^{-2} \text{ m}^3$. Compare with the value obtained using the ideal-gas expression.

(12.2) An empirical equation for describing a real gas, proposed by van der Waals, is

$$\left(p + \frac{N^2 a}{V^2}\right)(V - Nb) = NRT.$$

Write this equation in virial form and compare with Eq. (12.20).

12.3 The Boyle temperature of a real gas is the temperature for which the second virial coefficient is zero. Show that the Boyle temperature is equal to a/Rb . Compute the Boyle temperature for some of the gases listed in Table 12-1. [Note: The Boyle temperature is the temperature at which a real gas may be considered as obeying the ideal-gas equation, up to the second order of approximation.]

12.4 The coefficient of cubical expansion of a substance at constant pressure is defined as

$$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p.$$

Find β for (a) an ideal gas, and (b) a real

gas following the van der Waals equation given in Problem 12.2.

12.5 The bulk modulus of a substance at constant temperature is defined as

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T$$

Find κ_T for (a) an ideal gas, and (b) a real gas following the van der Waals equation given in Problem 12.2.

12.6 An empirical equation of state for real gases, proposed by Dieterici, is $p(V - nb)e^{Na/VRT} = nRT$. Write the equation in virial form and compare it with Eq. (12.20).

12.7 Express the equation for an isentropic process of an ideal gas in terms of: (a) pressure and temperature, (b) volume and temperature.

12.8 Show that the work done by an ideal gas during an isentropic (or reversible adiabatic) transformation is

$$nR(T_1 - T_2)/(\gamma - 1).$$

12.9 Compare the slopes of an isentropic and an isothermal transformation of an ideal gas at the same point in a p - V diagram. Conclude from the comparison that in an isentropic expansion of an ideal gas the temperature decreases. Explain why this is so.

12.10 Plot a Carnot cycle in a p - V diagram when the working substance is an ideal gas. Show that, if V_1 , V_2 , V_3 , and V_4 are the volumes of the gas at the end of each transformation, then

$$V_2/V_1 = V_3/V_4.$$

12.11 Compute the work done by the gas during each of the transformations composing a Carnot cycle, and show that the net work done is

$$W = nR(T_2 - T_1) \ln V_2/V_1.$$

Verify then that Eq. (11.47) is satisfied. [Hint: Use the result of Problem 12.10.]

12.12 The adiabatic compressibility of a substance is defined as

$$\kappa_s = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_s$$

Find κ_s for an ideal gas. The propagation of elastic waves in a gas is an adiabatic process and the velocity of propagation is given by $v = \sqrt{\kappa_s/\rho}$, where ρ is the density. Explain how, by measuring v , one can compute γ . Show that v depends only on the absolute temperature.

12.13 An ideal gas at 300°K occupies a volume of 0.5 m³ at a pressure of 2 atm. The gas expands adiabatically until its volume is 1.2 m³. Next the gas is compressed isobarically up to its original volume. Finally the pressure is increased isochorically until the gas returns to its initial state. (a) Plot the process in a p - V diagram. (b) Determine the temperature at the end of each transformation. (c) Find the work done during the cycle. Assume that $\gamma = 1.4$.

12.14 An ideal gas at 300°K occupies a volume of 0.5 m³ at a pressure of 2 atm. The gas expands adiabatically until its volume is 1.2 m³. Next the gas is compressed isothermally until the volume is the same as the original volume. Finally the pressure is increased isochorically until the gas returns to its initial state. (a) Plot the process in a p - V diagram. (b) Determine the temperature at the end of the adiabatic expansion. (c) Find the work done during the cycle. Assume that $\gamma = 1.4$.

12.15 An ideal gas is initially at $T_1 = 300^\circ\text{K}$, $p_1 = 3 \text{ atm}$, and $V_1 = 4 \text{ m}^3$. The gas expands isothermally to a volume of 16 m³. This is followed by an isochoric process to such a pressure that an adiabatic compression returns the gas to the original state. Assume that all the processes are

reversible, and do the following: (a) Draw the cycle on a p - V diagram and a T - S diagram, numerically labeling all end-points carefully. (b) Calculate the work done and the entropy change during each process and during the cycle. Assume that $\gamma = 1.4$.

12.16 Estimate the error made in evaluating Z_{rot} when $2l+1$ is replaced by $2l$ and $l(l+1)$ is replaced by l^2 in Eq. (12.32).

12.17 Calculate the percentage of molecules of a diatomic gas in the ground ($l = 0$) and first excited ($l = 1$) rotational states at temperatures $T = \Theta_r$ and $T = 2\Theta_r$.

12.18 Compare the number of hydrogen molecules per mole in the second excited rotational state ($l = 2$) with the number of chlorine molecules per mole for the same excited state when the temperature is 300°K.

12.19 Compare the number of hydrogen molecules per mole in the second excited vibrational state ($v = 2$) with the number of chlorine molecules per mole for the same excited state when the temperature is 300°K.

12.20 Consider a mole of CO gas. Calculate the number of molecules in the first three vibrational energy states at room temperature (300°K) and at 1000°K.

12.21 Show that the vibrational heat capacity of a gas at constant volume is given by

$$C_{V,\text{vib}} = R \left(\frac{\hbar\omega}{kT} \right)^2 \frac{e^{\hbar\omega/kT}}{(e^{\hbar\omega/kT} - 1)^2}.$$

Find the limiting values for $T \ll \Theta_v$ and $T \gg \Theta_v$.

12.22 Using the result of Problem 11.13, show that the entropy of a diatomic gas due to molecular rotations is

$$S_{\text{rot}} = kN[1 + \ln(T/\Theta_r)].$$

[Note: When the molecule is homonuclear, it can be shown that we must use $T/2\Theta_r$; this is due to a halving of the distinguishable states as a result of the symmetry of the molecule.]

12.23 Using the result of Problem 11.13, show that the entropy of a diatomic gas due to molecular vibrations is

$$S_{\text{vib}} = kN[(\Theta_v/T)(e^{\Theta_v/T} - 1) - \ln(1 - e^{-\Theta_v/T})].$$

Verify that for small temperatures S_{vib} tends to zero, while for large temperatures S_{vib} approaches the value

$$kN[1 + \ln(T/\Theta_v)].$$

Compare with the corresponding values for the molecules inside the oven and make a critical evaluation of the results of the experiment illustrated in Fig. 10-8. [*Hint*: Use the results of the preceding problem.]

10.31 (a) Show that the deBroglie wavelength for a particle of mass m moving with the most probable velocity of a maxwellian distribution at temperature T is $\lambda = h/(2mkT)^{1/2}$, where k is Boltzmann's constant. (b) Calculate the deBroglie wavelength of a neutron moving with the most probable speed of a maxwellian distribution at 20°C. Compare these wavelengths with the interatomic separation in a solid.

10.32 What fraction of (a) H atoms, and (b) HCl molecules would be in the first excited state at 300°K?

10.33 Suppose that the energy of the molecules of a system can be expressed as a sum of two terms; that is,

$$E_i = E_{i, \text{tr}} + E_{i, \text{int}}$$

where $E_{i, \text{tr}}$ refers to the translational motion and $E_{i, \text{int}}$ refers to the internal degrees of freedom (such as the rotation and vibration of a molecule), or to the interaction with an electric or magnetic field. If $g_{i, \text{tr}}$ and $g_{i, \text{int}}$ are the intrinsic probabilities corresponding to both types of motion, we have that $g_i = g_{i, \text{tr}} g_{i, \text{int}}$. Show that: (a) $Z = Z_{\text{tr}} Z_{\text{int}}$, where Z is the total partition function and Z_{tr} and Z_{int} are the translational and internal partition functions; (b) $U = U_{\text{tr}} + U_{\text{int}}$.

11 THERMODYNAMICS

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11.4 Many-Particle Systems; Heat

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3

ATOMS WITH ONE ELECTRON

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3.1 Introduction

We shall begin our study of atoms by summarizing our fundamental ideas about atomic structure. Every atom has an overall dimension of about 10^{-9} m. It is composed of a relatively massive nucleus (whose dimensions are of the order of 10^{-14} m) about which move a number of electrons, each of charge $-e$, occupying the rest of the atomic volume. The nucleus is composed of A particles (A is the mass number) called nucleons, of which Z are protons (Z is the atomic number), each of charge $+e$, and $N (= A - Z)$ are neutrons, which have no electric charge. Therefore the nucleus possesses a positive charge of $+Ze$. The number of electrons in any atom is equal to the number of protons (that is, Z of them) and therefore an atom is an electrically neutral system. However, in certain instances an atom may gain or lose some electrons, so that it becomes negatively or positively charged; in this case it is called an *ion*. The mass of the nucleon is about 1850 times the electron mass. Thus the mass of an atom is practically equal to that of its nucleus.

However, the Z electrons of an atom are responsible for most of the atomic properties which are reflected in the properties of matter in bulk, such as the elastic and electromagnetic properties of different materials. Electromagnetic interactions between electrons and nuclei of different atoms play the basic role in the binding together of atoms to form molecules, in chemical reactions, and in practically all the properties of matter in bulk.

We can explain the motion of the electrons around the nucleus if we consider only the electromagnetic interactions between the electrons and the components of the nucleus (protons and neutrons). Since electromagnetic interactions are well understood, it has been possible to develop an accurate description of the electronic motion. The corresponding problem for the nucleus, on the other hand, is more complex, since other interactions enter which are not so well understood. When we analyze electronic motion, we must use the methods of quantum mechanics discussed in the previous chapter.

In this chapter we shall discuss the properties of atoms and ions having just one electron (of which the simplest is the hydrogen atom) and in the following chapter we shall consider the problem of many-electron atoms. The one-electron atom will help us to understand the basic problems related to atomic structure.

3.2 The Hydrogen Atom

The simplest of all atoms is the hydrogen atom. Its nucleus is composed of only one particle, a proton, so that it has $A = 1$ and $Z = 1$. Around the proton, a single electron moves. So that our calculation will be applicable to other atoms we shall assume, however, that the nucleus contains Z protons with a total positive charge equal to $+Ze$ (Fig. 3-1). At this moment we shall make two approximations. First, we shall consider the nucleus to be at rest in an inertial system. This is a reasonable assumption because the nucleus, being more massive than the electron, practically coincides with the center of mass of the atom, which certainly is at rest in an inertial system so long as no external forces act on the atom. Second, we shall assume that the electric field of the nucleus is that of a point charge. This is also reasonable,

TABLE 3-1 Rydberg's Constant
($R_\infty = 10,973,731 \text{ m}^{-1}$)

Atom	Z	A	R, m^{-1}
Hydrogen (H)	1	1	10,967,758
Deuterium (D)	1	2	10,970,742
Tritium (T)	1	3	10,971,735
Helium (He^+)	2	4	10,972,227
Lithium (Li^{2+})	3	7	10,972,880
Beryllium (Be^{3+})	4	9	10,973,070

of mass. However, we can analyze the relative motion of the electron and the nucleus by substituting, in Eq. (3.4), the reduced mass of the electron-nucleus system for the electron mass. Given that M is the mass of the nucleus, then the reduced mass of the atom is*

$$\mu = \frac{m_e M}{m_e + M} = \frac{m_e}{1 + m_e/M}$$

Therefore in Eq. (3.5) we must replace Rydberg's constant R_∞ by

$$R = \frac{\mu e^4}{8\epsilon_0^2 h^3 c} = R_\infty \frac{\mu}{m_e} = R_\infty \left(\frac{1}{1 + m_e/M} \right), \quad (3.7)$$

so that the energy levels are given by $E = -RhcZ^2/n^2$. The value of R for several nuclei is given in Table 3-1. Obviously R_∞ corresponds to the case in which the nucleus has infinite mass ($M = \infty$), and this explains the reason for the subscript on the symbol.

So far we have considered only states of negative energy, or *bound states*. The states of positive energy, which in a classical description correspond to hyperbolic orbits, are *unbound states*, in which an electron with enough kinetic energy approaches the nucleus from a great distance and, after being deviated from its straight-line motion by its coulomb interaction with the nucleus, recedes again toward infinity. As explained in Section 2.7, positive energy states are not quantized, since the initial kinetic energy may have any arbitrary value and thus they form a continuum of states.

EXAMPLE 3.1. Semiclassical derivation of the expression for the energy levels of hydrogen.

Solution: We may justify Eq. (3.5) for the stationary states of the hydrogenlike atoms just as, at the end of Section 2.5, we justified the energy levels for a particle moving in a potential box by using concepts derived from our knowledge of standing waves. Let us suppose that the electron describes a circular orbit, as shown in Fig. 3-3. Its momentum p is constant for a circular orbit. In order that the orbit correspond to a stationary state,

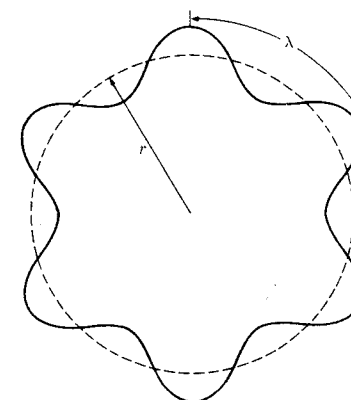


Fig. 3-3. Standing waves on a circle.

it seems logical that it must be able to sustain standing waves of wavelength $\lambda = h/p$. We can see from Fig. 3-3 that this requires that the length of the orbit be equal to an integral multiple of λ ; that is, $2\pi r = n\lambda = nh/p$, or

$$rp = nh/2\pi. \quad (3.8)$$

Noting that rp is the angular momentum of the electron, we see that the stationary states are those for which the angular momentum is an integral multiple of $\hbar = h/2\pi$. Since $p = m_e v$, we may also write Eq. (3.8) as

$$m_e v r = nh/2\pi. \quad (3.9)$$

On the other hand, the equation of motion for the electron requires that $F = m_e v^2/r$, where F is the centripetal force. But in the case of an electron moving about a nucleus, the centripetal force is the coulomb force given by Eq. (3.1). Therefore

$$\frac{m_e v^2}{r} = \frac{Ze^2}{4\pi\epsilon_0 r^2} \quad \text{or} \quad m_e v^2 = \frac{Ze^2}{4\pi\epsilon_0 r}. \quad (3.10)$$

When we eliminate v between Eqs. (3.9) and (3.10), we have

$$r = \frac{n^2 \hbar^2 \epsilon_0}{\pi m_e Z e^2} = \frac{n^2}{Z} a_0, \quad (3.11)$$

where

$$a_0 = \frac{\hbar^2 \epsilon_0}{\pi m_e e^2} = 5.2917 \times 10^{-11} \text{ m} \quad (3.12)$$

is called the *Bohr radius*. Expression (3.11) gives the radii of the allowed circular orbits, and the Bohr radius, a_0 , is the "radius" of the ground-state orbit ($n = 1$) in hydrogen ($Z = 1$).

When we use Eq. (3.2) for the potential energy of the electron-nucleus system, we may express the energy of the electron in a circular orbit as:

$$E = E_k + E_p = \frac{1}{2} m_e v^2 - \frac{Ze^2}{4\pi\epsilon_0 r}.$$

* See, for example, *Fundamental University Physics*, Volume I, Section 9.3.

Hence, if we use Eq. (3.10) to eliminate $m_e v^2$, we obtain

$$E = -\frac{Ze^2}{4\pi\epsilon_0(2r)} \quad (3.13)$$

Introducing the value of r as given by Eq. (3.11), we have

$$E = -\frac{m_e e^4 Z^2}{8\epsilon_0^2 h^2 n^2} = -\frac{R_\infty hc Z^2}{n^2},$$

which agrees with Eqs. (3.4) and (3.6). However, a word of caution concerning our derivation: Besides being applicable only to circular orbits, it all depends on the validity of Eq. (3.8), which we shall discuss in more detail later (Section 3.4). On the other hand, the concept of orbit must be considered here as applying to the region in which the electron is most likely to be found, and Eq. (3.11) is only an indication of the magnitude of the region in which the electron moves most of the time, and thus of the size of the atom.

Combining Eqs. (3.9) and (3.11), we find that the velocity of the electron in a stationary orbit is

$$v = \frac{nh}{2\pi m_e r} = \frac{hZ}{2\pi m_e a_0 n} = \frac{21.9 \times 10^5 Z}{n} \text{ m s}^{-1}.$$

We must consider this result as indicating only the order of magnitude of the velocity of the electron. Note that the velocity decreases when the energy increases (larger value of n). Also we have that $v/c \sim 7 \times 10^{-3} Z/n$, and thus $v \ll c$, except for large values of Z and small values of n . Hence relativistic corrections are not very important except when great accuracy is desired. However, these corrections are very important from the theoretical point of view.

EXAMPLE 3.2. Estimate the magnitude of the correction term in Eq. (3.7), due to the nuclear motion, for the energy of the stationary states of the lightest atoms; that is, H, D, T, He^+ , and Li^{2+} .

Solution: Since m_e/M is a very small quantity, we may, by using the approximation $(1+x)^{-1} = 1 - x + \dots$, write Eq. (3.7) as

$$R = R_\infty \left(1 - \frac{m_e}{M}\right) \quad \text{or} \quad \Delta R = R - R_\infty = -\frac{m_e}{M} R_\infty.$$

The mass of an atom of mass number A can be written, to a good approximation, as $M = 1.67 \times 10^{-27} A$ kg and $m_e = 9.11 \times 10^{-31}$ kg. Thus $m_e/M = 5.45 \times 10^{-4}/A$. Therefore since the energy is proportional to R , we may write

$$\frac{\Delta E}{E} = -\frac{m_e}{M} = -100 \frac{m_e}{M} \% = -\frac{5.45 \times 10^{-2}}{A} \%,$$

where ΔE is the change in energy from the value given in Eq. (3.5). The results for the lightest elements are indicated in Table 3-2.

The fact that $\Delta E/E$ is different for H, D, and T means that the energy levels for these three hydrogen isotopes are slightly displaced, resulting in what is called an *isotopic effect*. Similarly, the even levels of He^+ do not exactly coincide with those of H. It was this minor difference that led to the discovery of helium by Frankland and Lockyer when they analyzed the solar spectrum in 1868.

TABLE 3-2 Energy Corrections When Nuclear Motion Is Considered

Atom	H	D	T	He^+	Li^{2+}
A	1	2	3	4	7
$(m_e/M) \times 10^4$	5.45	2.75	1.82	1.36	0.78
$-(\Delta E/E), \%$	0.0545	0.0275	0.0182	0.0136	0.0078

3.3 The Spectrum of Hydrogen

As we saw in Fig. 3-2, the energy of the stationary states increases with the quantum number n . The difference in energy between the levels corresponding to n_1 and n_2 (with $n_2 > n_1$) for a hydrogenlike ion is

$$E_2 - E_1 = \left(-\frac{RhcZ^2}{n_2^2}\right) - \left(-\frac{RhcZ^2}{n_1^2}\right) = RhcZ^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

When we apply Bohr's condition, $\nu = (E_2 - E_1)/h$ (Eq. 1.29), and neglect recoil effects, the frequency of the electromagnetic radiation emitted or absorbed by the atom in a transition between states corresponding to n_1 and n_2 is

$$\begin{aligned} \nu &= \frac{E_2 - E_1}{h} = R_c Z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \\ &= 3.2899 \times 10^{15} Z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \text{ Hz.} \end{aligned} \quad (3.14)$$

Spectroscopists sometimes prefer to use the *wave number* $\tilde{\nu} = \nu/c = 1/\lambda$, rather than the frequency.* Their reasoning is that spectroscopic measurements usually determine wavelength and not frequency. The wave number in the MKSC system is given in m^{-1} , although the most common unit is cm^{-1} . In this case the above equation becomes

$$\tilde{\nu} = RZ^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) = 1.0974 \times 10^5 Z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \text{ cm}^{-1}.$$

This expression (or the preceding one) is called *Balmer's formula*, and is applicable only to hydrogenlike atoms. Since in a spectroscope (either prism or grating) each transition appears as a line (which is the image of the slit), the spectrum is called a *line spectrum*, and frequently the words line and transition are used as synonyms.

* The wave number $\tilde{\nu}$ gives the number of wavelengths in one unit of length, and it should not be confused with the wave number $k = 2\pi/\lambda$, which is associated with a particle, and which was defined in Section 1.10.

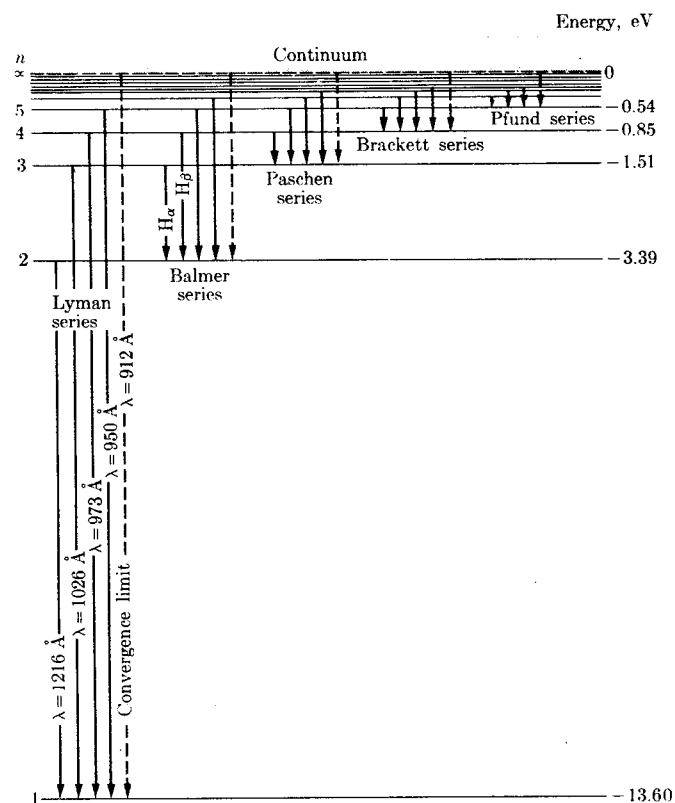


Fig. 3-4. Radiative transitions in hydrogen.

The hydrogen spectrum ($Z = 1$) (and similarly for the spectra of other atoms) is classified in terms of series, each series formed by transitions that have the lowest energy level in common. Figure 3-4 represents the following hydrogen series:

- (1) Lyman series: $n_1 = 1, n_2 = 2, 3, 4, \dots$
- (2) Balmer series: $n_1 = 2, n_2 = 3, 4, \dots$
- (3) Paschen series: $n_1 = 3, n_2 = 4, 5, \dots$
- (4) Brackett series: $n_1 = 4, n_2 = 5, 6, \dots$
- (5) Pfund series: $n_1 = 5, n_2 = 6, 7, \dots$

The Balmer series, which is mostly in the visible region, is easily observed with a common spectroscope. The Lyman series falls in the ultraviolet region and the others in the infrared. The transitions indicated in Fig. 3-4 correspond to the emission spectrum; the reverse transitions take place in the absorption spectrum.

Historically, the problem of explaining the line spectra of hydrogen and other elements was what caused the first application of the quantum theory to the atom. The Swiss mathematician J. Balmer (1825–1898), long before the advent of the quantum theory, empirically obtained formula (3.14) in 1885, without any theoretical explanation related to atomic structure. In 1913 the Danish physicist Niels Bohr, then at Cambridge University, derived Eq. (3.14) by introducing, for the first time, the concept of stationary states. Since quantum mechanics had not yet been formulated, Bohr's method consisted of a series of *ad hoc* assumptions closely resembling the calculations made in Example 3.1.

EXAMPLE 3.3. Determine the first excitation potential and the ionization energy of hydrogen.

Solution: As we explained when we discussed the Franck-Hertz experiment in Section 1.8, the first excitation potential is the energy required to take an atom from its ground state to its first (or lowest-lying) excited state. These states in hydrogenlike atoms correspond, respectively, to $n = 1$ and $n = 2$. Setting $n = 1$ and $n = 2$ in Eq. (3.6) with $Z = 1$, we have $E_1 = -13.6$ eV and $E_2 = -3.4$ eV. Thus the energy required to excite the atom from the ground state to the first excited state is $E_2 - E_1 = 10.2$ eV. If a hydrogen atom is carried to its first excited state by an inelastic electron collision, as happens in a gas discharge tube, it returns to the ground state by emitting radiation of frequency

$$\nu = (E_2 - E_1)/h = 2.47 \times 10^{15} \text{ Hz}$$

or wavelength

$$\lambda = 1.216 \times 10^{-7} \text{ m},$$

which in this case falls in the ultraviolet region. The ionization energy is the energy required to take the electron from the ground state ($n = 1$) to the state of zero energy ($n = \infty$), and thus is equal to $-E_1 = 13.6$ eV. Ionization may result from either an inelastic collision of the hydrogen atom with an electron or another charged particle, with another atom, or from the atom's absorbing a photon having a frequency equal to or larger than 3.29×10^{15} Hz or a wavelength equal to or shorter than 9.12×10^{-8} m.

3.1 Quantization of Angular Momentum

So far we have seen that the energy of an atomic system is quantized. We must explore the possibility that some other physical quantities are also quantized; i.e., restricted to only certain values for the system. We noted at the end of Section 2.5 that the momentum of a particle in a potential box is also quantized. In most examples in Chapter 2 the momentum and/or the energy were constants of the motion; i.e., quantities whose value does not change during the motion of the particle. It is reasonable then to inquire whether or not other constants of the motion are quantized.

We know that for motion under central forces, the angular momentum $\mathbf{L} = \mathbf{r} \times \mathbf{p}$ relative to the center of force is a constant of the motion. In quantum mechanics this is also true. A careful theoretical and experimental analysis shows that the

TABLE 3-3 Designation of Angular Momentum States and Essential Degeneracy for Motion Under Central Forces

Angular momentum, l	0	1	2	3	4	5
Symbol	s	p	d	f	g	h
Degeneracy, $g = 2l + 1$	1	3	5	7	9	11

angular momentum is quantized; i.e., it may have only discrete values. It can be shown (see Example 3.4) that the magnitude of the angular momentum is characterized by the values

$$L^2 = l(l+1)\hbar^2, \quad (3.15)$$

where $l = 0, 1, 2, 3, \dots$ is a positive integer. However, in hydrogenlike atoms the values of l for each energy level are limited by the values of n corresponding to the energy level, and the maximum value of l is $n - 1$. Therefore

in a coulomb field, for each value of n , specifying an energy level, there are n distinct values of the angular momentum from $l = 0$ to $l = n - 1$.

It is customary to designate the possible values of l by means of letters, according to the scheme of Table 3-3. Therefore for $n = 1$ we have $l = 0$ or s; for $n = 2$ we have $l = 0$ and 1 or s and p. For $n = 3$, it is $l = 0, 1$, and 2 or s, p, and d, etc.

In a central field different from the coulomb field the values of l associated with each energy level are also different. For example, in the case of a three-dimensional oscillator the potential energy is $E_p = \frac{1}{2}kr^2$. The possible energy levels are $E = (n + \frac{3}{2})\hbar\omega$ (see Eq. 2.22), and for each n the l values are $n, n - 2, n - 4, \dots, 1$ or 0. Then for $n = 0$ we have $l = 0$ or s; for $n = 1$, $l = 1$ or p; for $n = 2$, $l = 0$ and 2 or s and d, and so on.

In addition to its limitation with regard to its magnitude, experimental evidence (to be discussed later) indicates that the angular momentum is restricted in direction, a situation called space quantization. This means that the angle L makes with the Z -axis (Fig. 3-5) is not arbitrary; in other words, it can be shown (see Example 3.4) that the values of the component L_z are quantized and given by

$$L_z = m_l \hbar, \quad (3.16)$$

where $m_l = 0, \pm 1, \pm 2, \pm 3, \dots, \pm l$; that is, m_l is a positive or negative integer from 0 to l . The quantum number m_l cannot be larger than l because L_z would then be larger than $|L|$, which is impossible. Therefore we conclude that:

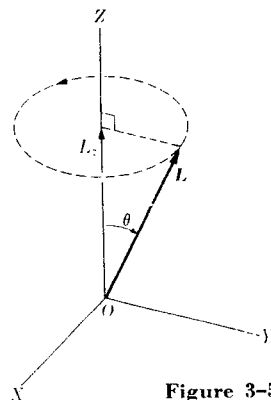


Figure 3-5

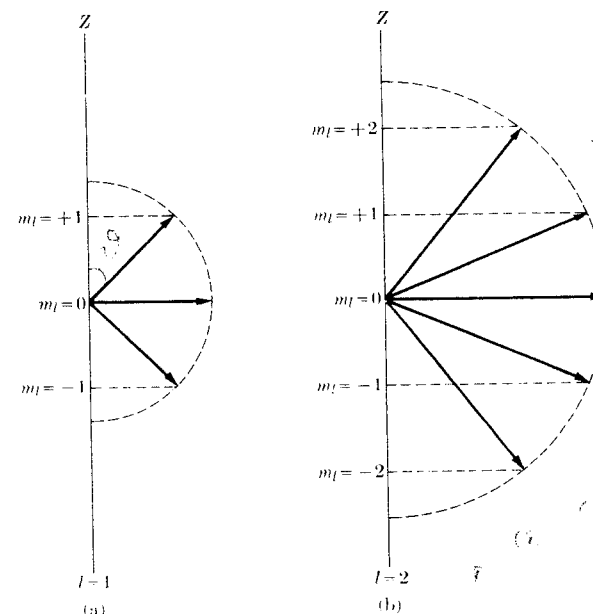


Fig. 3-6. Space quantization illustrated for $l = 1$ and $l = 2$.

for each value of the angular momentum, there are $2l + 1$ values of m_l or $2l + 1$ different orientations of L .

Figure 3-6 illustrates this situation for $l = 1$ and $l = 2$. The quantity $g = 2l + 1$ is called the essential degeneracy of the angular momentum state. It can be proved that this degeneracy is a consequence of the spherical symmetry of the motion under a central force. The values of g for a few angular momentum values are given in Table 3-3.

In classical mechanics the angular momentum under a central force is constant in magnitude and direction. However, in quantum mechanics, the magnitude of the angular momentum is given by Eq. (3.15) and of one of its components by Eq. (3.16). But to specify the direction of the angular momentum, we need to know the two other components, L_x and L_y . A detailed analysis, which will not be reproduced here because of its mathematical complexity, shows that

it is impossible to know, exactly, more than one component of the angular momentum.

Therefore, if we know L_z , our knowledge of L_x and L_y is at best within the uncertainties ΔL_x and ΔL_y , which satisfy the uncertainty relation

$$\Delta L_x \Delta L_y \geq \frac{1}{2} \hbar L_z.$$

This relation is similar to the uncertainty relations for position and momentum (Eq. 1.48), and for energy and time (Eq. 1.49). In other words,

in quantum mechanics, it is impossible to precisely determine the direction of the angular momentum.

Since we can know only $|L|$ and L_z , we may picture the angular momentum vector L in Fig. 3-5 as precessing around the Z -axis, at a constant angle θ .

From this discussion we may conclude that the energy levels of hydrogenlike atoms are somewhat more complex than the simple picture implied in Eq. (3.6) and Fig. 3-2. In a coulomb field each energy level, corresponding to a given n , contains n different angular momentum states, all with the same energy and with l ranging from zero to $n - 1$ (this is shown in Fig. 3-7). These levels are indicated by ns , np , nd , etc. (This result agrees with the classical description of motion under an inverse-square force, for which the energy is independent of the angular momentum, although the eccentricity of the elliptical orbits depends on the angular momentum.) In a more refined theory of one-electron atoms which takes into account other effects (such as relativistic corrections), the different angular momentum states corresponding to the same n appear with different energies.

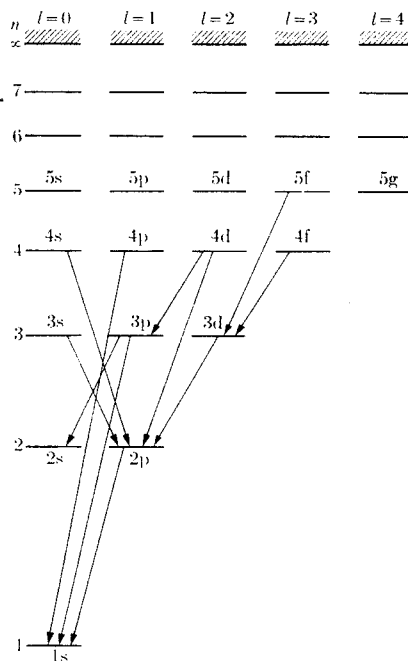


Fig. 3-7. Transitions among different angular momentum states.

If the force is not inverse-square, those levels which have the same value of n but different angular momenta (i.e., levels ns , np , nd , etc.) do not necessarily all have the same energy. Thus under central forces, the energy depends in general on n and l , but it cannot depend on m_l , since in a central field of force the orientation of the orbit is irrelevant.

The fact that each level in a hydrogenlike atom is composed of several angular momentum states is, however, important from the point of view of the transitions. For motion in a central-force potential, the selection rules for electric-dipole transitions are

$$\Delta l = \pm 1, \quad \Delta m_l = 0, \pm 1. \quad (3.17)$$

These selection rules are imposed by the law of conservation of angular momentum, since the emitted or absorbed photon carries angular momentum; therefore the angular momentum of the atom must change to compensate for the angular momentum carried by the emitted or absorbed photon. The law of conservation of angular momentum and the quantum rule for addition of angular momenta (see Section 3.8) would allow $\Delta l = 0, \pm 1$. However, the parity of the wave functions in a central potential (to be discussed in Section 3.5) forbids the possibility that $\Delta l = 0$.

The selection rules (3.17) require that transitions occur only between angular momentum states in adjacent columns of Fig. 3-7. Some of these possible transitions have been indicated. Note that, according to these rules, the state $2s$ cannot change into state $1s$, which is the only lower-lying level available. For that reason the state $2s$ is called a *metastable state*. The rules (3.17) are valid for electric-dipole transitions, which are the most probable. For other transitions, such as magnetic-dipole or electric-quadrupole transitions, the selection rules are different; these transitions have a much lower probability than electric-dipole transitions. For this reason, in atomic spectra, usually only electric-dipole transitions are taken into account.

Let us now comment on Eq. (3.8). Noting that for a circular orbit rp is the angular momentum L , we see that Eq. (3.8) reads $L = n\hbar$. But this result disagrees with Eq. (3.15), which is $L = \sqrt{l(l+1)}\hbar$. Hence the simple and intuitive model used in Example 3.1 for obtaining Eq. (3.8) is incorrect (although the result obtained is correct). This again warns the student that it is not possible, unless one takes great care, to extrapolate wave concepts when they are applied to quantum mechanics. In this case of angular momentum, the discrepancy is due to the fact that it is impossible to confine the electron waves to a strict circular path. However, setting $l = n - 1$ in Eq. (3.15), we get

$$L^2 = (n-1)n\hbar^2 = (n^2 - n)\hbar^2.$$

If n is large we may approximate this expression by writing $L^2 = n^2\hbar^2$ or $L = n\hbar$, which agrees with Eq. (3.8). Thus $l = n - 1$ with n large approximates the classical circular orbits. This is an illustration of Bohr's correspondence principle, which states that for large quantum numbers the quantum description approaches the classical description.

3.5 One-Electron Wave Functions Under Central Forces

The wave function $\psi(x, y, z)$ for hydrogenlike atoms is obtained by solving Schrödinger's equation, Eq. (3.3). The potential energy which appears in that equation, $E_p = -Ze^2/4\pi\epsilon_0 r$, corresponds to a central force. We may expect that the wave functions of all central-force problems [i.e., problems in which the potential energy is only a function of the distance and therefore has the form $E_p(r)$] have a certain similarity.

Because of the spherical symmetry of the potential energy, we can simplify the discussion of central-force problems by using the spherical coordinates r, θ, ϕ

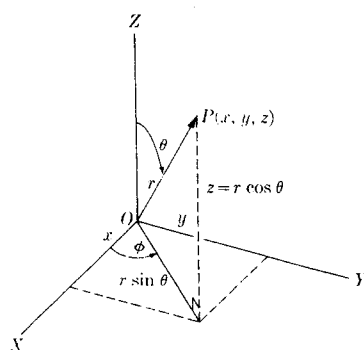
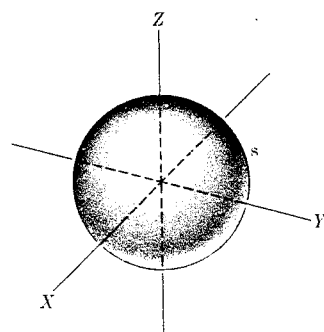


Fig. 3-8. Spherical coordinates.

Fig. 3-9. Angular wave function for s-states ($l = 0$).

(Fig. 3-8). We can show that the wave function for a single electron in a central field can be written as a product of two factors, one that depends on the distance of the electron from the origin and another that depends on the orientation of the position vector \mathbf{r} , given by the angles θ and ϕ . Thus we may write the wave function as

$$\psi(r, \theta, \phi) = R(r)Y(\theta, \phi).$$

The radial part $R(r)$ depends on the particular form of the potential energy $E_p(r)$ corresponding to the force acting on the electron. However, since the angular part $Y(\theta, \phi)$ is a consequence of the spherical symmetry of the central force, it is independent of the particular form of the potential energy $E_p(r)$. In other words, the angular functions $Y(\theta, \phi)$ are the same for all central-force problems.

We shall not analyze how to obtain the wave functions, although it is a straightforward mathematical problem (see Example 3.4). Instead we shall discuss the most important properties of the wave functions.

In a central-force problem the angular part of the wave function is determined entirely by the magnitude and the Z-component of the angular momentum of the electron.

The magnitude of the angular momentum is determined by the quantum number l and the Z-component or orientation is determined by m_l . For that reason the angular functions corresponding to specific values of L^2 and L_z will be designated as $Y_{lm_l}(\theta, \phi)$. Mathematicians call these functions *spherical harmonics*.

Table 3-4 gives the angular functions Y_{lm_l} for $l = 0, 1$, and 2 . This is the form which is applicable to most physical problems. Table 3-5 gives the angular functions in a form more suitable to the discussion of molecular binding. The functions in Table 3-5 do not belong to a particular value of m_l , but of m_l^2 or $|m_l|$, and they correspond to L^2 and L_z^2 instead of L_z .

TABLE 3-4 Angular Functions Corresponding to L^2 and L_z

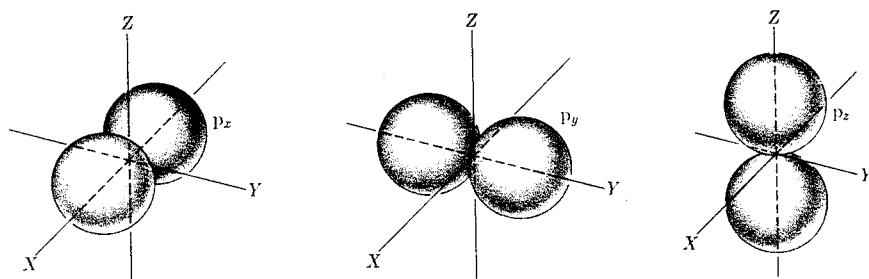
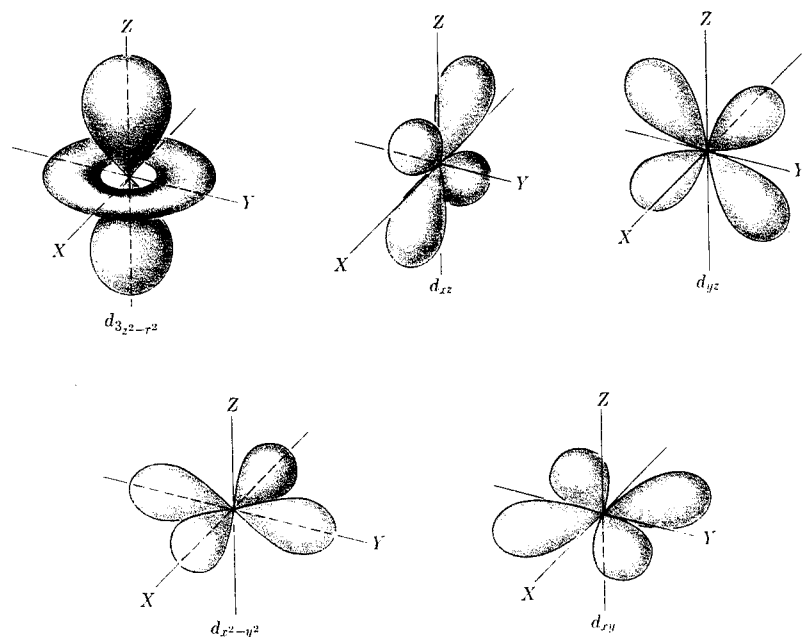
l	m_l	Angular function
0	0	$Y_{00} = 1/\sqrt{4\pi}$
1	0	$Y_{10} = \sqrt{3/4\pi} \cos \theta$
	± 1	$Y_{1\pm 1} = \mp \sqrt{3/8\pi} \sin \theta e^{\pm i\phi}$
2	0	$Y_{20} = \frac{1}{2}\sqrt{5/4\pi} (3 \cos^2 \theta - 1)$
	± 1	$Y_{2\pm 1} = \mp \sqrt{15/8\pi} \sin \theta \cos \theta e^{\pm i\phi}$
	± 2	$Y_{2\pm 2} = \frac{1}{4}\sqrt{15/2\pi} \sin^2 \theta e^{\pm i2\phi}$

TABLE 3-5 Angular Functions Corresponding to L^2 and L_z^2

l	$ m_l $	Angular function
0	0	$s = 1/\sqrt{4\pi}$
1	0	$p_z = \sqrt{3/4\pi} \cos \theta$
	1	$p_x = \sqrt{3/4\pi} \sin \theta \cos \phi$ $p_y = \sqrt{3/4\pi} \sin \theta \sin \phi$
2	0	$d_{3z^2-r^2} = \sqrt{5/16\pi} (3 \cos^2 \theta - 1)$
	1	$d_{xz} = \sqrt{15/4\pi} \sin \theta \cos \theta \cos \phi$ $d_{yz} = \sqrt{15/4\pi} \sin \theta \cos \theta \sin \phi$
	2	$d_{x^2-y^2} = \sqrt{15/4\pi} \sin^2 \theta \cos 2\phi$ $d_{xy} = \sqrt{15/4\pi} \sin^2 \theta \sin 2\phi$

From Table 3-5 we can see that for $l = 0$ (or s-states), the only wave function is independent of the angles; that is, s-states are *spherically symmetric*. We can see this in the polar diagram of Fig. 3-9, where the value of the s-function for each direction (θ, ϕ) is indicated by the length of a line from the origin. The locus of the end points results in a spherical surface. This result is understandable because, if the angular momentum is zero, there is no preferred orientation of the electron's orbit.

For $l = 1$ (or p-states), there are three angular functions, representing the three possible orientations of the angular momentum or the three values of $m_l = 0, \pm 1$. Table 3-5 designates them as p_x, p_y , and p_z and they are shown in the polar diagrams of Fig. 3-10. These functions correspond to a preferred motion of the

Fig. 3-10. Angular wave functions for p-states ($l = 1$).Fig. 3-11. Angular wave functions for d-states ($l = 2$).

electron along each of the coordinate axes, a result that is very important for describing chemical binding.

For $l = 2$ (or d-states), there are five different angular functions. The angular distribution of these states is more complex, as we can see from the polar diagrams of Fig. 3-11, which represent the d-functions of Table 3-5. For larger values of l , the situation becomes even more complex.

TABLE 3-6 Radial Wave Functions of Hydrogenlike Atoms

n	l	$R_{nl}(r)$ ($\rho = 2Zr/na_0$)
1	0	$R_{10}(r) = 2 \left(\frac{Z}{a_0} \right)^{3/2} e^{-\rho/2}$
2	0	$R_{20}(r) = \frac{1}{2\sqrt{2}} \left(\frac{Z}{a_0} \right)^{3/2} (2 - \rho) e^{-\rho/2}$
	1	$R_{21}(r) = \frac{1}{2\sqrt{6}} \left(\frac{Z}{a_0} \right)^{3/2} \rho e^{-\rho/2}$
3	0	$R_{30}(r) = \frac{1}{9\sqrt{3}} \left(\frac{Z}{a_0} \right)^{3/2} (6 - 6\rho + \rho^2) e^{-\rho/2}$
	1	$R_{31}(r) = \frac{1}{9\sqrt{6}} \left(\frac{Z}{a_0} \right)^{3/2} \rho(4 - \rho) e^{-\rho/2}$
	2	$R_{32}(r) = \frac{1}{9\sqrt{30}} \left(\frac{Z}{a_0} \right)^{3/2} \rho^2 e^{-\rho/2}$

An important property of the angular functions Y_{lm} is that they have a parity equal to $(-1)^l$. That is, for $l = 0, 2, 4, \dots$, even integer, the functions Y_{lm} have the same value and sign at points symmetrically situated relative to the origin of coordinates, and thus are even functions, while for $l = 1, 3, 5, \dots$, odd integer, the functions Y_{lm} have the same value but opposite signs at symmetric points, and are odd functions. It can be shown that for electric-dipole transitions the initial and final states must have opposite parities, and therefore these states cannot have the same value of l . For that reason the value $\Delta l = 0$ is impossible for these transitions, as previously indicated in connection with Eq. (3.17).

The radial part $R(r)$ of the wave function $\psi(r, \theta, \phi)$ depends on the energy and the magnitude of the angular momentum, but not on its orientation. We can understand this because the spherical symmetry of a central field indicates that the radial distribution of the electron's motion must be independent of the orientation of its angular momentum; that is, it must be independent of the value of m_l . This is the quantum analog of the classical result that the energy and the magnitude of the angular momentum determine the "size" of the orbit. Therefore the radial function depends on the quantum number n associated with the energy, and on l , but not on m_l . Thus these radial functions are written as $R_{nl}(r)$, and the total wave functions become

$$\psi_{nlm_l}(r, \theta, \phi) = R_{nl}(r) Y_{lm_l}(\theta, \phi). \quad (3.18)$$

Table 3-6 gives the radial functions corresponding to the first three energy levels of hydrogenlike atoms. These functions are shown in Fig. 3-12. The dashed line in each case indicates the classical radius of the orbit, in accordance with Eq. (3.11).

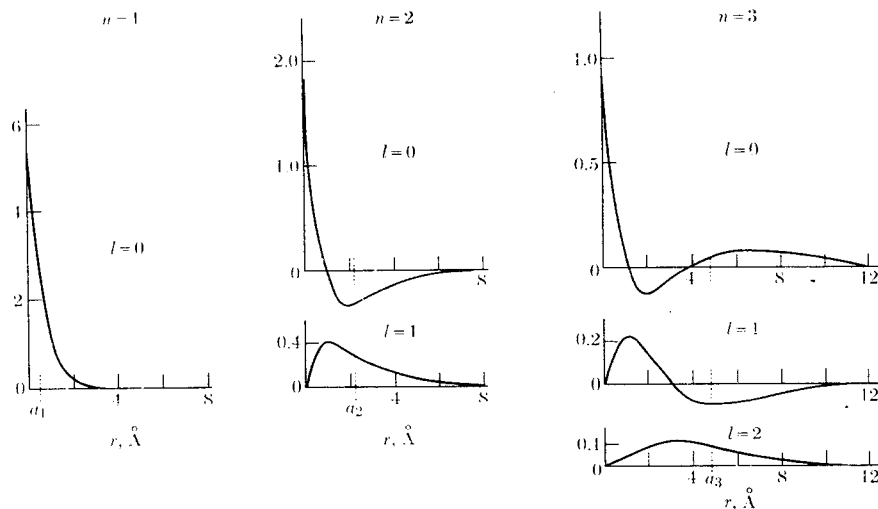


Fig. 3-12. Radial wave functions of hydrogen for $n = 1, 2$, and 3 . The ordinate of the curves in each case is $[R_{nl}(r) \text{ m}^{-3/2}] \times 10^{-8}$.

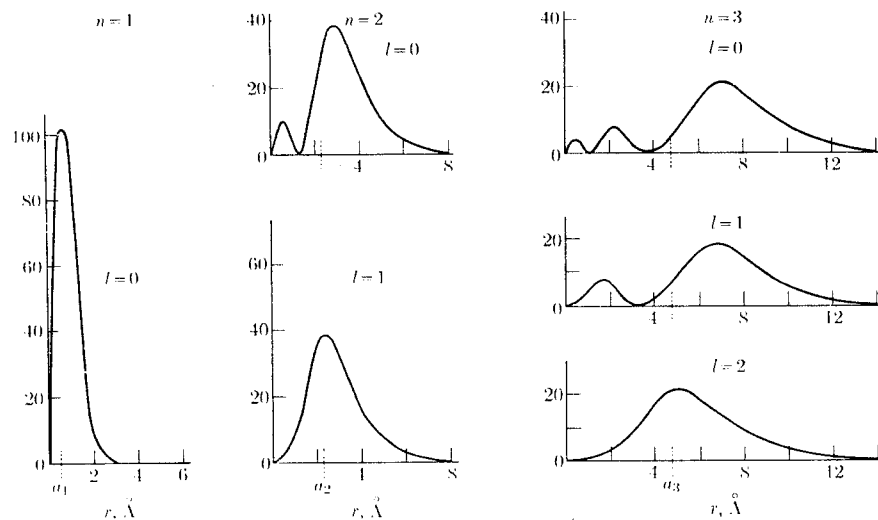


Fig. 3-13. Radial probability distribution in hydrogen for $n = 1, 2$, and 3 . The ordinate in each case is $[r^2 R_{nl}(r) \text{ m}^{-1}] \times 10^{-15}$.

We can see that, although the electron is most likely to be found within the classical radius of the orbit, it may also be found at larger distances. The probability of finding the electron within a spherical shell of radii r and $r + dr$, regardless of its angular position, is proportional to $r^2 [R_{nl}(r)]^2$ (see Problem 3.25). Figure 3-13 shows these probabilities.

One interesting peculiarity, easily appreciated by looking at Fig. 3-12, is that the radial functions for s-electrons are relatively large for small r . We say that the s-electrons describe penetrating orbits reaching very close to the nucleus. The p-electrons are less penetrating, the d-electrons even less so, and so on for higher values of the angular momentum. This is easy to understand if we consider that (in both classical and quantum mechanics) the radial motion under a central force corresponds to an effective potential

$$E_{p,\text{eff}} = E_p(r) + \frac{L^2}{2mr^2} = E_p(r) + \frac{l(l+1)\hbar^2}{2mr^2}, \quad (3.19)$$

where $E_p(r)$ is the potential energy of the central force (the coulomb potential in the case of an electron) and $L^2/2mr^2$ is called the centrifugal potential (see Example 3.5). For s-states we have $l = 0$ and there is no centrifugal potential, so that $E_{p,\text{eff}} = E_p$. Thus a bound s-electron with negative energy E (Fig. 3-14a) can classically move between O and A , and therefore has access to the origin of coordinates. The shape of the radial part of the wave function must then be as shown at the bottom of the figure. (The number of oscillations of the wave function depends on the energy.) But for other values of the angular momentum, the shape of the effective potential is as shown in Fig. 3-14(b). Therefore an electron of energy E must move classically between B and C . We translate this into quantum-mechanical language by stating that the wave function must decrease very rapidly outside the classical limits of motion, and must therefore be very small near the origin. The larger the angular momentum, the further the wave function is pushed away from the origin and the less "penetrating" is the orbit.

This characteristic of electron motion is reflected in many important properties of the atom. For example, s-electrons are very sensitive to the shape and internal structure of the nucleus, while electrons with larger angular momentum are much less sensitive to nuclear shape and structure.

EXAMPLE 3.4. Analysis of angular momentum operators and proper functions.

Solution: We recall from Table 2-4, Section 2.12, that the angular momentum operator is given by

$$\mathbf{L} = -i\hbar \mathbf{r} \times \nabla = -i\hbar \begin{vmatrix} \mathbf{u}_x & \mathbf{u}_y & \mathbf{u}_z \\ x & y & z \\ \partial/\partial x & \partial/\partial y & \partial/\partial z \end{vmatrix}$$

from which we conclude that the Z-component is

$$L_z = -i\hbar \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right), \quad (3.20)$$

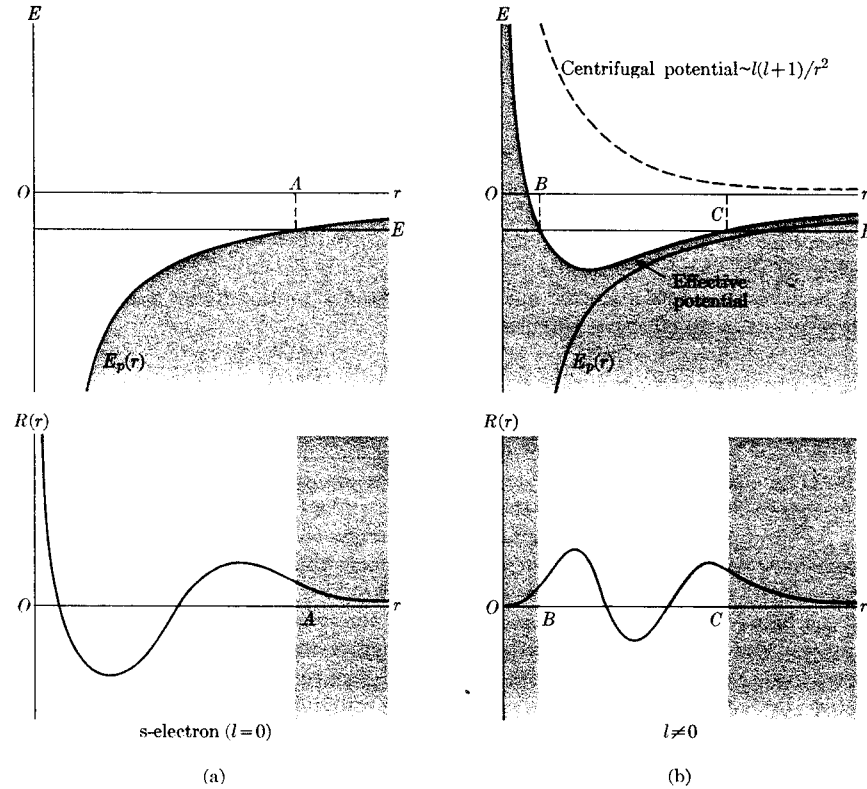


Fig. 3-14. Effective potential and radial wave function for $l = 0$ and $l \neq 0$ for motion under a central force.

with similar expressions for L_x and L_y . It is more convenient to express L_z in terms of spherical coordinates. Noting from Fig. 3-8 that

$$x = r \sin \theta \cos \phi, \quad y = r \sin \theta \sin \phi, \quad z = r \cos \theta,$$

we have that

$$\frac{\partial}{\partial \phi} = \frac{\partial x}{\partial \phi} \frac{\partial}{\partial x} + \frac{\partial y}{\partial \phi} \frac{\partial}{\partial y} + \frac{\partial z}{\partial \phi} \frac{\partial}{\partial z}.$$

But $\partial x / \partial \phi = -r \sin \theta \sin \phi = -y$, $\partial y / \partial \phi = r \sin \theta \cos \phi = x$, and $\partial z / \partial \phi = 0$. Therefore

$$\frac{\partial}{\partial \phi} = -y \frac{\partial}{\partial x} + x \frac{\partial}{\partial y},$$

and the operator L_z can be written in the form

$$L_z = -i\hbar \frac{\partial}{\partial \phi}. \quad (3.21)$$

It can be shown that this relation is absolutely general and that the quantum operator corresponding to the component of the angular momentum along any direction is given by $-i\hbar \partial / \partial \phi$, where ϕ is an angle measured around the direction. The proper equation, according to Eq. (2.48), is $L_z \Phi = L_z \Phi$, where $\Phi(\phi)$ is the proper function and L_z the proper value. Therefore, using Eq. (3.21) for L_z , we obtain

$$-i\hbar \frac{\partial \Phi}{\partial \phi} = L_z \Phi \quad \text{or} \quad \frac{\partial \Phi}{\partial \phi} = im_l \Phi,$$

where we have set $m_l = L_z / \hbar$ or $L_z = m_l \hbar$. The solution of this equation is $\Phi = C e^{im_l \phi}$ where C is the normalization constant. Since the same point of space is represented by ϕ and by $\phi + 2\pi$, it is necessary that $\Phi(\phi) = \Phi(\phi + 2\pi)$, which means that $e^{im_l \phi} = e^{im_l(\phi + 2\pi)}$ or $e^{i2\pi m_l} = 1$. This requires that m_l be a positive or negative integer; that is, $m_l = 0, \pm 1, \pm 2, \dots$, as indicated previously in Section 3.4. To determine C , we apply the normalization condition, which in this case becomes $\int_0^{2\pi} \Phi^* \Phi d\phi = 1$ or

$$\int_0^{2\pi} (C^* e^{-im_l \phi}) (C e^{im_l \phi}) d\phi = |C|^2 \int_0^{2\pi} d\phi = 2\pi |C|^2 = 1,$$

or, assuming C is real, $C = 1/\sqrt{2\pi}$. Therefore the normalized proper functions of the Z -component of the angular momentum are

$$\Phi(\phi) = \frac{1}{\sqrt{2\pi}} e^{im_l \phi}, \quad m_l = 0, \pm 1, \pm 2, \dots, \quad (3.22)$$

and the proper values $L_z = m_l \hbar$ are integral multiples of \hbar .

The square of the magnitude of the angular momentum is given by the operator $L^2 = L_x^2 + L_y^2 + L_z^2$, where L_x and L_y are operators similar to L_z , as given by Eq. (3.20). Transforming to spherical coordinates, by means of an elaborate algebraic manipulation, shows that the square of the angular momentum is represented by the quantum operator

$$L^2 = -\hbar^2 \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right]. \quad (3.23)$$

The proper equation is $L^2 Y(\theta, \phi) = L^2 Y(\theta, \phi)$, where the proper function, which depends on the angles θ and ϕ , has been designated by $Y(\theta, \phi)$ and the proper value is L^2 . This corresponds to the differential equation

$$\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 Y}{\partial \phi^2} + \frac{L^2}{\hbar^2} Y = 0.$$

It can be shown that to obtain a solution satisfying the requirements of quantum mechanics, it is necessary that $L^2 / \hbar^2 = l(l+1)$, where l is a positive integer; that is, $l = 0, 1, 2, 3, \dots$. In this form we have obtained the results previously stated in

Section 3.5; that is, $L^2 = l(l+1)\hbar^2$. The solutions of the resulting equation,

$$\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 Y}{\partial \phi^2} + l(l+1)Y = 0,$$

are designated by Y_{lm_l} and are the functions given in Table 3-4. The table shows that the functions Y_{lm_l} are the products of one factor depending on θ and another depending on ϕ . [The ϕ -factor is identical to Eq. 3.22.] That is, $Y_{lm_l} = P_l^{m_l}(\cos \theta) e^{im_l\phi}$. Considering that the Y_{lm_l} are proper functions of the operators L^2 and L_z , we may then write

$$L^2 Y_{lm_l} = l(l+1)\hbar^2 Y_{lm_l}, \quad L_z Y_{lm_l} = m_l \hbar Y_{lm_l}.$$

EXAMPLE 3.5. Analysis of Schrödinger's equation for motion under central forces.

Solution: We recall from Eq. (2.9) that Schrödinger's equation for motion with a potential energy $E_p(r)$ is

$$-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \psi + E_p(r)\psi = E\psi.$$

If we now change from the rectangular coordinates x, y, z to the spherical coordinates r, θ, ϕ , this equation, after a lengthy algebraic manipulation, becomes

$$-\frac{\hbar^2}{2m} \left\{ \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} + \frac{1}{r^2} \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] \right\} \psi + E_p(r)\psi = E\psi.$$

Recalling Eq. (3.23) for the operator L^2 , we may write

$$-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} - \frac{L^2}{\hbar^2 r^2} \right) \psi + E_p(r)\psi = E\psi.$$

If we set $\psi = R(r)Y_{lm_l}(\theta, \phi)$ and recognize that $L^2 Y_{lm_l} = l(l+1)\hbar^2 Y_{lm_l}$, the above equation becomes

$$-\frac{\hbar^2}{2m} \left[\frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} - \frac{l(l+1)}{r^2} \right] R + E_p(r)R = ER.$$

This is an equation that contains only the radial part $R(r)$ of the wave function ψ . It is customary to set $R(r) = u(r)/r$, resulting in

$$-\frac{\hbar^2}{2m} \frac{d^2 u}{dr^2} + \left[E_p + \frac{l(l+1)\hbar^2}{2mr^2} \right] u = Eu. \quad (3.24)$$

This is sometimes called the *radial Schrödinger equation*. Comparing this equation with the one-dimensional Schrödinger equation (2.3), we conclude that the radial motion is equivalent to a one-dimensional motion under an effective potential energy given by Eq. (3.19); that is,

$$E_{p,\text{eff}} = E_p(r) + \frac{l(l+1)\hbar^2}{2mr^2}.$$

The term $E_{p,\text{cen}} = l(l+1)\hbar^2/2mr^2$ is a centrifugal potential because the corresponding "force," $F = -\partial E_{p,\text{cen}}/\partial r$ is positive and hence is directed away from the origin.

When we set $E_p(r) = -Ze^2/4\pi\epsilon_0 r$, we obtain a differential equation that admits as solutions, for motion under coulomb forces, the radial functions given in Table 3-6. For other forms of the potential energy, different radial functions result.

EXAMPLE 3.6. Relativistic correction of the energy in hydrogenlike atoms.

Solution: As we explained in Section 2.12, Schrödinger's equation (3.3) is obtained by means of the nonrelativistic expression $E = p^2/2m_e + E_p$. This procedure is correct whenever the velocity of the electron is very small compared with the velocity of light. The value of v/c for an electron in a stationary state was estimated in Example 3.1 and found to be of the order of $7 \times 10^{-3}Z/n$. The relativistic effect due to this velocity, although very small, can easily be detected by spectroscopic methods. The relativistic energy of an electron moving with momentum p and having a potential energy E_p (see Eq. A.11) is

$$E = c\sqrt{m_e^2 c^2 + p^2} + E_p - m_e c^2,$$

where the rest mass energy has been subtracted so that the zero of energy coincides with the nonrelativistic case. Assuming that the momentum p is much smaller than $m_e c$, we may expand the radical up to the second-order term, resulting in

$$\begin{aligned} E &= \frac{1}{2m_e} p^2 - \frac{1}{8m_e^3 c^2} p^4 + \cdots + E_p \\ &= \left(\frac{1}{2m_e} p^2 + E_p \right) - \frac{1}{8m_e^3 c^2} p^4 + \cdots \end{aligned} \quad (3.25)$$

The two terms inside the parentheses give the nonrelativistic approximation for the energy. Therefore the last term is the first-order relativistic correction to the total energy of the electron, which we shall designate by ΔE_r . Thus

$$\Delta E_r = -\frac{1}{8m_e^3 c^2} p^4 = -\frac{1}{2m_e c^2} \left(\frac{p^2}{2m_e} \right) \left(\frac{p^2}{2m_e} \right).$$

The identical terms inside the parentheses correspond to the nonrelativistic kinetic energy of the electron. So (as a reasonable approximation) we may write for the first one, using the result of Eqs. (3.10) and (3.13),

$$\frac{p^2}{2m_e} = \frac{1}{2} m_e v^2 = -\frac{Ze^2}{4\pi\epsilon_0(2r)} + \frac{Ze^2}{4\pi\epsilon_0 r} = \frac{Ze^2}{4\pi\epsilon_0(2r)} = -E.$$

For the second, we may write $p^2/2m_e = \frac{1}{2} m_e v^2$. Therefore

$$\Delta E_r = -\frac{1}{2m_e c^2} \left(-E \right) \left(\frac{1}{2} m_e v^2 \right) = \frac{1}{4} \frac{v^2}{c^2} E.$$

Thus the relativistic correction is of the order of $(v/c)^2$ times the energy of the electron. In the hydrogen atom, for example, $(v/c)^2$ is of the order of 10^{-5} , and therefore $\Delta E_r \sim 10^{-5}E$, or about 0.001% of E , a quantity which, although small, can easily be detected in the laboratory with experimental techniques now in use.

To obtain a more precise result, we note that the last term in Eq. (3.25), which we have just seen is very small compared with the first two, may be considered as a small perturbation. To compute its effect on the stationary states, we may estimate its average or expectation value, according to Eq. (2.50). Therefore in the state described by the wave function ψ_{nlm_l} we have

$$\Delta E_r = -\frac{1}{8m_e c^2} (p^4)_{\text{ave}} = -\frac{1}{8m_e c^2} \int \psi_{nlm_l}^* p^4 \psi_{nlm_l} d\tau.$$

The result of this calculation is

$$\Delta E_r = \frac{|E_n| Z^2 \alpha^2}{n} \left(\frac{3}{4n} - \frac{1}{l + \frac{1}{2}} \right), \quad (3.26)$$

where

$$\alpha = e^2/4\pi\epsilon_0\hbar c \approx 1/137$$

is called the *fine structure constant* and $|E_n|$ is the absolute value of the energy as given by Eq. (3.5). The energy levels, in our approximation, are thus given by $E = E_n + \Delta E_r$. Since the relativistic correction (3.26) depends on l as well as on n , levels having the same n but different l do not have the same energy. In other words, the relativistic correction destroys the accidental degeneracy we found in the case of a coulomb field. Also the relativistic correction is always negative for all n and l . For a given n , the smaller the value of l , the larger the relativistic correction. Thus the states for which the correction is most important in hydrogen are 1s and 2s.

A more refined relativistic theory of the electron has been developed by P. A. M. Dirac. In Dirac's theory, from the outset, a Schrödinger equation corresponding to the relativistic energy is set up, and in this way the exact energy levels are obtained. However, his theory is too complicated to be presented here.

3.6 The Zeeman Effect

Space quantization manifests itself in a striking way when the electronic motion is disturbed by an applied magnetic field. Under a sufficiently strong magnetic field, each spectral line in a one-electron atom becomes a triplet, consisting of three closely spaced lines. The spacing is the same for all atoms and lines and is proportional to the magnitude of the magnetic field. This effect was observed for the first time in 1896 by the Dutch physicist Pieter Zeeman (1865–1943). It has been named the *Zeeman effect*, to honor his work.

An electron describing a circular orbit with an angular velocity ω passes each point in the orbit $\omega/2\pi$ times per second and therefore corresponds to a current $I = e(\omega/2\pi)$. Since the current loop is very small, it is equivalent to a magnetic dipole whose magnetic moment is equal to current times area. Therefore, the *orbital magnetic dipole moment* of the electron is

$$M_L = e(\omega/2\pi)(\pi r^2) = \frac{1}{2}e\omega r^2.$$

Recalling that for a circular orbit $L = m_e v r = m_e \omega r^2$, we have $M_L = (e/2m_e)L$. This is a relation between the magnitudes of M_L and L . Now the direction of L is related to the direction of motion of the electron, as shown in Fig. 3-15. On the other hand, the charge of the electron is negative, and therefore the equivalent

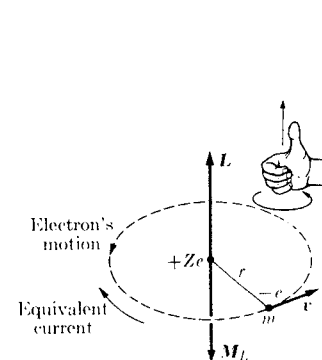


Fig. 3-15. Relation between the orbital magnetic moment and the angular momentum of an electron.

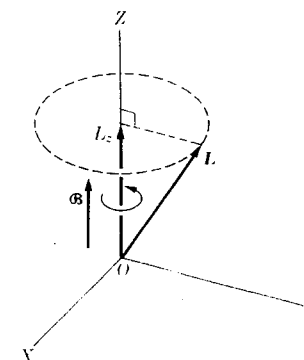


Fig. 3-16. Precession of the angular momentum under the action of a magnetic field.

current is opposite to that of the electron motion, resulting in an orientation of M_L which is opposite to that of L . Thus we may write the vector equation

$$\mathbf{M}_L = -\frac{e}{2m_e} \mathbf{L}. \quad (3.27)$$

Although we have obtained this relation for a circular orbit and have used classical mechanics, this expression still holds true in quantum mechanics for an arbitrary motion with angular momentum L . The Z-component of the orbital magnetic moment is

$$M_{Lz} = -\frac{e}{2m_e} L_z = -\frac{e\hbar}{2m_e} m_l = -\mu_B m_l, \quad (3.28)$$

where the quantity

$$\mu_B = \frac{e\hbar}{2m_e} = 9.2732 \times 10^{-24} \text{ J T}^{-1} = 5.6564 \times 10^{-5} \text{ eV T}^{-1} \quad (3.29)$$

is called a *Bohr magneton*.

When a magnetic dipole of moment \mathbf{M} is placed in a magnetic field \mathbf{B} , it acquires an energy $E_B = -\mathbf{M} \cdot \mathbf{B}$. Therefore, when an atom is placed in a magnetic field, the additional energy of an orbiting electron due to the external magnetic field is

$$E_B = -\mathbf{M}_L \cdot \mathbf{B} = \frac{e}{2m_e} \mathbf{L} \cdot \mathbf{B}. \quad (3.30)$$

At the same time, the electron experiences a torque

$$\boldsymbol{\tau} = \mathbf{M}_L \times \mathbf{B} = -\frac{e}{2m_e} \mathbf{L} \times \mathbf{B},$$

which makes the angular momentum L precess around the direction of the magnetic field \mathbf{B} , as indicated in Fig. 3-16. Taking the Z-axis parallel to the magnetic field \mathbf{B} ,

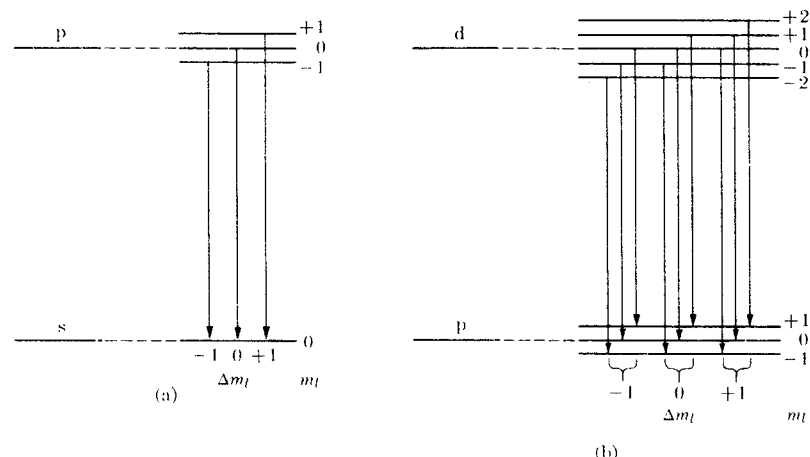


Fig. 3-17. Splitting of s-, p-, and d-energy levels under the action of a magnetic field. The separation of successive levels is $\mu_B \mathcal{B}$.

we can rewrite Eq. (3.30) as $E_{\mathcal{B}} = -M_{Lz}\mathcal{B}$ or, using Eq. (3.28), we have

$$E_{\mathcal{B}} = \mu_B \mathcal{B} m_l \quad (3.31)$$

We then see that $E_{\mathcal{B}}$, instead of having a continuous range of values, may have $2l + 1$ distinct values corresponding to each of the $2l + 1$ possible orientations of \mathbf{L} relative to \mathcal{B} , all equally spaced by the amount $\mu_B \mathcal{B}$.

The total energy of an electron bound to an atom placed in magnetic field is $E_n + E_{\mathcal{B}}$, where E_n is the energy of the electron's motion in the absence of a magnetic field. Therefore Eq. (3.31) indicates that each energy level with quantum numbers n, l splits into $2l + 1$ levels in the presence of a magnetic field. The separation between successive levels is also reflected in the frequencies associated with the transitions between the levels. The situation for s-, p-, and d-levels is illustrated in Fig. 3-17. States with $l = 0$ (or s-states) are not affected by the magnetic field. States with $l = 1$ (or p-states) are split into three equally spaced states, corresponding to orientations in which $m_l = +1, 0$, and -1 . Thus the transition $p \rightarrow s$ becomes a triple transition, one corresponding to $m_l = 0 \rightarrow m_l = 0$, with the original frequency, and two others corresponding to $m_l = \pm 1 \rightarrow m_l = 0$, with a frequency difference given by

$$\Delta\nu = \pm \frac{\mu_B \mathcal{B}}{h} = 1.40 \times 10^{10} \mathcal{B} \text{ Hz.} \quad (3.32)$$

So each of the single lines $p \rightarrow s$ shown in Fig. 3-8 becomes three closely spaced lines. Similarly, states with $l = 2$ (or d-states) are split into five equally spaced

levels corresponding to the orientations of \mathbf{L} given by $m_l = \pm 2, \pm 1, 0$. The transition $d \rightarrow p$ now has nine possibilities, according to the selection rule $\Delta m_l = \pm 1, 0$. However, transitions corresponding to the same value of Δm_l all have the same energy change and therefore yield the same spectral line. We then conclude that although there are nine possible transitions, the spectrum of the $d \rightarrow p$ transition under a magnetic field contains only three lines, with $\Delta\nu$ still given by Eq. (3.32).

The quantization of angular momentum clearly explains the experimental facts of the Zeeman effect. If instead of space quantization, the angular momentum could have any orientation, the effect of the magnetic field would be to broaden each level. The new levels would then occupy an energy band of width $2\mu_B \mathcal{B} L$ and each line would become a band. This is why, as we mentioned before, the Zeeman effect is a proof of space quantization. In fact, the Zeeman effect was one of the phenomena that prompted introducing the idea of the quantization of angular momentum.

3.7 Electron Spin

Let us recall that the earth, in addition to its orbital motion around the sun, has a rotational or spinning motion about its axis. Therefore the total angular momentum of the earth is the vector sum of its orbital angular momentum and its spin angular momentum. By analogy we may suspect that a bound electron in an atom is also spinning. However, we cannot describe the electron as a spherical spinning particle because of our ignorance of its internal structure. Thus we cannot compute the spin angular momentum of the electron in the same way that we compute the spin angular momentum of the earth in terms of its radius and angular velocity. The idea of electron spin was first proposed in 1926 by G. Uhlenbeck and S. Goudsmit to explain certain features of the spectra of one-electron atoms (we shall consider these in Section 3.9). If \mathbf{S} is the spin angular momentum of an electron and \mathbf{L} is the orbital angular momentum, the total angular momentum is $\mathbf{J} = \mathbf{L} + \mathbf{S}$. For given values of \mathbf{L} and \mathbf{S} , the value of \mathbf{J} depends on their relative orientation, and we may expect this to be reflected in certain atomic properties; this indeed is the case.

The existence of electron spin is borne out by a large accumulation of experimental evidence. For example, electron spin is manifested in a very direct way by the Stern-Gerlach experiment, first performed in 1924. Because the electron is a charged particle, electron spin should result in an intrinsic or spin magnetic dipole moment \mathbf{M}_S of the electron. If the electron could be described as a rotating rigid charged body, the relation between \mathbf{M}_S and \mathbf{S} would be the same as between \mathbf{M}_L and \mathbf{L} , as given by Eq. (3.27). However, this is not so, and we must write

$$\mathbf{M}_S = -g_s \frac{e}{2m_e} \mathbf{S},$$

where g_s is called the gyromagnetic ratio of the electron. The experimental value for g_s is 2.0024. For most practical purposes, we can make $g_s = 2$. The total

magnetic dipole moment of an orbiting and spinning electron is therefore

$$\mathbf{M} = \mathbf{M}_L + \mathbf{M}_S = -\frac{e}{2m_e}(\mathbf{L} + g\mathbf{S}), \quad (3.33)$$

and, of course, depends not only on the magnitudes of \mathbf{L} and \mathbf{S} but also on their relative orientation.

Suppose now that a beam of hydrogenlike atoms is passed through an inhomogeneous magnetic field, as shown in Fig. 3-18. The effect of such a magnetic field on a magnetic dipole is to exert a force whose direction and magnitude depend on the relative orientation of the magnetic field and the magnetic dipole. For example, if the magnetic dipole is oriented parallel to the magnetic field, it tends to move in the direction in which the magnetic field increases, while if the magnetic dipole is oriented antiparallel to the magnetic field, it will move in the direction in which the magnetic field decreases.

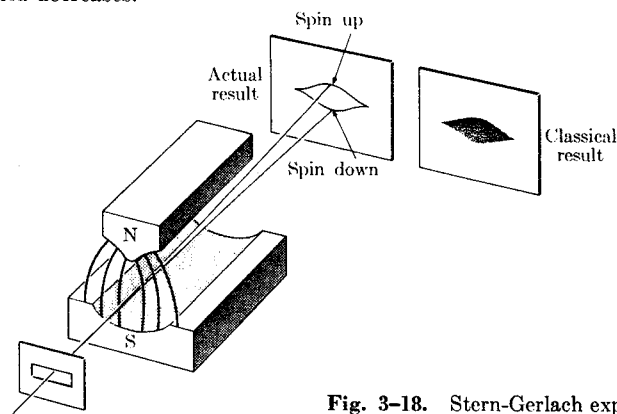


Fig. 3-18. Stern-Gerlach experiment.

In the Stern-Gerlach experiment the inhomogeneous magnetic field is produced by shaping the pole faces as shown in Fig. 3-18. The magnetic field increases in strength in the S-N direction. If the hydrogenlike atoms are in their ground state, the orbital angular momentum of the electron is zero (s-state or $l = 0$) and the entire magnetic moment is due to the spin. Therefore the atomic beam will be deviated by the magnetic field, depending on the orientation of \mathbf{M}_S , or, which is equivalent, the orientation of \mathbf{S} . The result of the experiment is that the atomic beam is split in two by the inhomogeneous magnetic field. This shows that

the electron spin may have only two orientations relative to the magnetic field: either parallel or antiparallel.

Since, according to our discussion in Section 3.4, the number of orientations of an angular momentum vector relative to a fixed Z-axis is $g = 2l + 1$, for the case of spin we have the value $g = 2$ or $l = \frac{1}{2}$. Designating the spin quantum number by s instead of l and the quantum number corresponding to the component S_z by m_s ,

we then have that $s = \frac{1}{2}$ and $m_s = \pm \frac{1}{2}$. Then

$$\begin{aligned} S^2 &= s(s+1)\hbar^2 = \frac{3}{4}\hbar^2, & s &= \frac{1}{2}, \\ S_z &= m_s\hbar, & m_s &= \pm \frac{1}{2}. \end{aligned} \quad (3.34)$$

The only two permitted values of m_s (that is, $+\frac{1}{2}$ and $-\frac{1}{2}$), corresponding to the two possible orientations of \mathbf{S} , are shown in Fig. 3-19. For brevity they are usually referred to as *spin up* (\uparrow) and *spin down* (\downarrow), although the spin is never actually directed along the Z-axis or opposite to it.

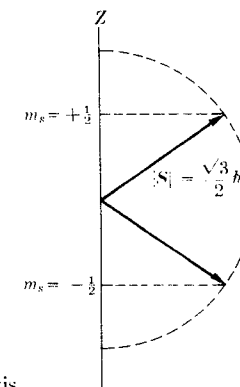


Fig. 3-19. Possible orientations of the spin relative to the Z-axis.

We shall designate the wave function associated with the S_z -component of the spin by χ_{m_s} . The exact form of χ_{m_s} is of no concern to us; its main properties are that

$$S^2\chi_{m_s} = \frac{3}{4}\hbar^2\chi_{m_s}, \quad S_z\chi_{m_s} = m_s\hbar\chi_{m_s}.$$

Sometimes we use, instead of χ_{m_s} , the notation χ_+ and χ_- , corresponding respectively to $m_s = +\frac{1}{2}$ and $-\frac{1}{2}$. Then the complete wave function of an electron moving in a central field is

$$\psi_{nlm_l m_s} = R_{nl}(r)Y_{lm_l}(\theta, \phi)\chi_{m_s}. \quad (3.35)$$

Note from Eq. (3.35) that, to completely describe the state of an electron in a central field, four quantum numbers are required: n , l , m_l , and m_s .

The properties of the electron spin, described by Eq. (3.34), cannot be explained in terms of any classical model of the electron. However, we can explain them theoretically when we combine the ideas of quantum mechanics with the principle of relativity. This was done by Dirac around 1928, but we shall not discuss his analysis here, since it is beyond the scope of this book.

When the atom is in a state in which $l \neq 0$, the splitting produced by the magnetic field depends on the total magnetic moment, or—which is the same thing—on the total angular momentum $\mathbf{J} = \mathbf{L} + \mathbf{S}$. Therefore the Stern-Gerlach experiment can be used to determine the total angular momentum of the state of an atom.

3.8 Addition of Angular Momenta

In the previous section we saw that the resultant angular momentum \mathbf{J} of an electron in a hydrogenlike atom is the sum of the orbital angular momentum \mathbf{L} and the spin angular momentum \mathbf{S} ; that is, $\mathbf{J} = \mathbf{L} + \mathbf{S}$. It is important to examine the possible values of \mathbf{J} according to quantum mechanics. So that our analysis may be generally applicable, let us suppose that we have two angular momenta, designated by \mathbf{J}_1 and \mathbf{J}_2 , which may, for example, correspond to the orbital angular momentum

of an electron and its spin (as we have just considered in the preceding section), or the angular momentum of two electrons in an atom (a case which we shall consider in the next chapter). Then $J_1^2 = j_1(j_1 + 1)\hbar^2$, $J_{1z} = m_1\hbar$, and $J_2^2 = j_2(j_2 + 1)\hbar^2$, $J_{2z} = m_2\hbar$. It can be shown that in the most general case j_1 and j_2 can be either integers or half integers; that is, $0, \frac{1}{2}, 1, \frac{3}{2}, 2, \dots$. As explained before, orbital angular momenta can only be integers.

If $\mathbf{J} = \mathbf{J}_1 + \mathbf{J}_2$ is the resultant angular momentum, so that $J_z = J_{1z} + J_{2z}$,

then

$$J^2 = j(j+1)\hbar^2, \quad J_z = m\hbar, \quad m = \pm j, \pm(j-1), \dots \quad (3.36)$$

with $m = m_1 + m_2$. But because \mathbf{J}_1 and \mathbf{J}_2 may have different relative orientations, there are several possible values of J . Thus we find that the quantum number j varies in unit-sized steps from $j_1 + j_2$ down to $|j_1 - j_2|$, so that it can attain only the values

$$j = j_1 + j_2, \quad j_1 + j_2 - 1, \quad j_1 + j_2 - 2, \dots, \quad |j_1 - j_2|.$$

The first value corresponds to \mathbf{J}_1 and \mathbf{J}_2 "parallel" and the last value to the two angular momenta "antiparallel." Successive values of j differ by one unit, and if $j_2 \leq j_1$, the total number of possibilities is $2j_2 + 1$.

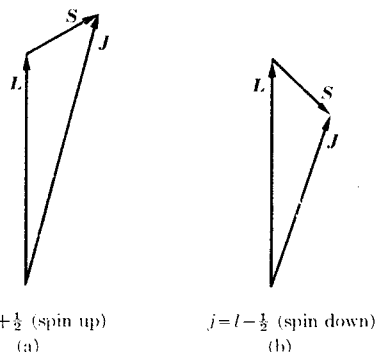


Fig. 3-20. Possible relative orientations of \mathbf{L} and \mathbf{S} , when $l = 2$.

For example, if $j_2 = \frac{1}{2}$, the possible values of j are $j_1 + \frac{1}{2}$ and $j_1 - \frac{1}{2}$, corresponding to parallel and antiparallel orientations. Thus, in the case of an electron if $\mathbf{J}_1 = \mathbf{L}$ and $\mathbf{J}_2 = \mathbf{S}$, we have that the possible values of the total angular momentum \mathbf{J} are $j = l \pm \frac{1}{2}$. These two situations are illustrated in Fig. 3-20 for $l = 2$. Hence we have that

the electron spin may have only two possible orientations relative to the orbital angular momentum.

When $l = 0$ (or s-state) only $j = \frac{1}{2}$ is possible. When we indicate the value of j as a subscript, the possible states of an electron in a central field are designated as shown in Table 3-7.

TABLE 3-7 Designation of Electronic States

l	0	1	2	3
j	$\frac{1}{2}$	$\frac{1}{2}, \frac{3}{2}$	$\frac{3}{2}, \frac{5}{2}$	$\frac{5}{2}, \frac{7}{2}$
Symbol	s _{1/2}	p _{1/2} , p _{3/2}	d _{3/2} , d _{5/2}	f _{5/2} , f _{7/2}

As another illustration, if $j_2 = 1$ and $j_1 > 1$, then $j = j_1 + 1, j$, or $j_1 - 1$. It may be shown that in an electric dipole transition the photon carries an angular momentum corresponding to a j -value of 1. Then if j_1 refers to the orbital angular momentum l of the electron and $j_2 = 1$ to that of the photon, the allowed values of the orbital angular momentum of an electron after emitting or absorbing the photon are $l + 1, l$, and $l - 1$, corresponding to $\Delta l = \pm 1, 0$. As we explained previously in Section 3.4, $\Delta l = 0$ is ruled out by parity considerations.

3.9 Spin-Orbit Interaction

The double orientation of the electron spin relative to the orbital angular momentum gives rise to an important effect: the doubling of energy levels (except s-levels) of hydrogenlike atoms. This doubling of levels in turn gives rise to a doubling of the spectral lines. These lines appear in pairs, having frequencies or wavelengths which are very close and are therefore called doublets. The best-known doublet is that composed of the two yellow or D-lines of sodium, corresponding to wavelengths of 5890 Å and 5896 Å. In fact, it was the problem of explaining these doublets which first gave rise to the idea of an electron spin with two possible orientations.

The doubling of the energy levels is a consequence of the so-called spin-orbit interaction. The origin of this interaction is as follows: in a frame of reference XYZ attached to the nucleus of an atom, the electron appears to revolve around the nucleus (Fig. 3-21a) with angular momentum \mathbf{L} . But, in a frame of reference $X'Y'Z'$ attached to the electron it is the nucleus which appears to revolve around

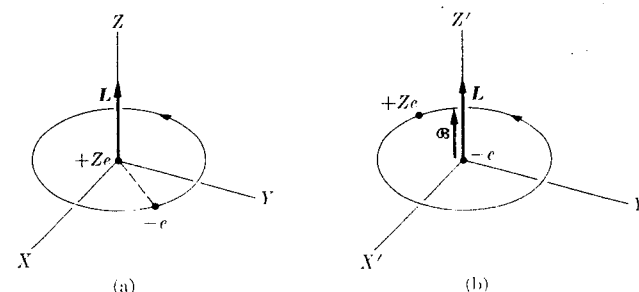


Fig. 3-21. Origin of the spin-orbit interaction.

the electron. The nucleus, since it has a positive charge, produces a magnetic field \mathbf{B} in the $X'Y'Z'$ frame which is parallel to the angular momentum \mathbf{L} . Since the electron is at rest relative to $X'Y'Z'$, the only interaction of the nuclear magnetic field is with the electron-spin magnetic moment \mathbf{M}_S . This interaction is proportional to $\mathbf{M}_S \cdot \mathbf{B}$. But \mathbf{B} is parallel to \mathbf{L} and \mathbf{M}_S is parallel to \mathbf{S} . Therefore the interaction is proportional to $\mathbf{S} \cdot \mathbf{L}$. This is why this effect is called spin-orbit interaction. We may then write, for the energy of the electron due to the spin-orbit interaction,

$$E_{SL} = a\mathbf{S} \cdot \mathbf{L}, \quad (3.37)$$

where a is a quantity which depends on the different variables affecting the electron's motion and whose precise form we need not know at this time. Given that E_n is the energy of the electronic motion, assuming only a central force, then the total energy, when the spin-orbit interaction is added, is

$$E = E_n + E_{SL} = E_n + a\mathbf{S} \cdot \mathbf{L}. \quad (3.38)$$

P.R. When we write this expression we assume that the spin-orbit interaction does not affect the contribution to the energy due to the central forces, a valid assumption so long as E_{SL} is very small compared with E_n . For a given value of \mathbf{L} and \mathbf{S} , the spin-orbit interaction E_{SL} depends on the relative orientation of these two vectors. But since \mathbf{S} can have only two possible orientations relative to \mathbf{L} , we conclude that

the spin-orbit interaction splits each electron energy level with a given value of l into two closely spaced levels.

One level corresponds to \mathbf{L} and \mathbf{S} parallel or spin up ($j = l + \frac{1}{2}$), and the other to \mathbf{L} and \mathbf{S} antiparallel or spin down ($j = l - \frac{1}{2}$). Obviously s-levels ($l = 0$) remain single.

In the presence of a spin-orbit interaction the quantum numbers needed to specify the angular momentum state of an electron are l , j , and m , where m refers to the proper value of J_z . The selection rules for electric-dipole transitions, required by the conservation of angular momentum are

$$\Delta l = \pm 1, \quad \Delta j = 0, \pm 1, \quad \Delta m = 0, \pm 1. \quad (3.39)$$

The transitions with $\Delta j = 0$ are very weak because they require a reversal of the direction of the spin relative to the orbital angular momentum of the electron. But the force that would produce such spin reversal is the spin-orbit interaction, which is a relatively weak force.

Figure 3-22 depicts (not to scale) how the levels shown in Fig. 3-7 are affected by the spin-orbit interaction, and some of the possible transitions. The relatively weak transition $d_{3/2} \rightarrow p_{3/2}$ is indicated by a dashed line. We see that spectral lines corresponding to transitions between s- and p-levels are therefore doublets, while those between d- and p-levels are triplets, although one of the lines is so weak that one may speak of a doublet.

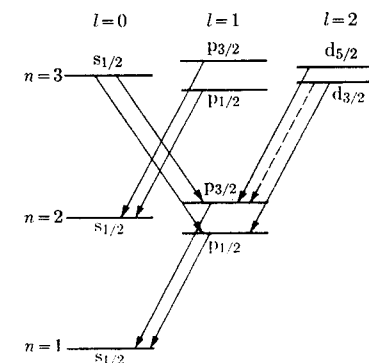


Fig. 3-22. Spin-orbit splitting of energy levels and possible transitions. The dashed line indicates a transition with very low probability.

EXAMPLE 3.7. Calculation of the separation of two energy levels due to the spin-orbit interaction.

Solution: Our purpose is to compute the value of E_{SL} for the two cases of spin up and spin down, and find their difference. This difference gives the splitting of the energy levels. To do this, we must find $\mathbf{S} \cdot \mathbf{L}$ in both cases. Now $\mathbf{J} = \mathbf{L} + \mathbf{S}$ and therefore $\mathbf{J}^2 = \mathbf{L}^2 + \mathbf{S}^2 + 2\mathbf{S} \cdot \mathbf{L}$, from which we obtain

$$\mathbf{S} \cdot \mathbf{L} = \frac{1}{2}(\mathbf{J}^2 - \mathbf{L}^2 - \mathbf{S}^2).$$

Inserting the values of \mathbf{L}^2 , \mathbf{S}^2 , and \mathbf{J}^2 , as given by Eqs. (3.15), (3.34), and (3.36), we obtain

$$\mathbf{S} \cdot \mathbf{L} = \frac{1}{2}\{j(j+1) - l(l+1) - \frac{3}{4}\}\hbar^2$$

or

$$\mathbf{S} \cdot \mathbf{L} = \begin{cases} \frac{1}{2}\hbar^2, & \text{spin up, } j = l + \frac{1}{2}, \\ -\frac{1}{2}(l+1)\hbar^2, & \text{spin down, } j = l - \frac{1}{2}. \end{cases}$$

Thus, when we use Eq. (3.38), the energy levels become

$$\begin{cases} E(\uparrow) = E_n + E_{SL}(\uparrow) = E_n + \frac{1}{2}a\hbar^2, & j = l + \frac{1}{2}, \\ E(\downarrow) = E_n + E_{SL}(\downarrow) = E_n - \frac{1}{2}a(l+1)\hbar^2, & j = l - \frac{1}{2}. \end{cases}$$

Thus, if a is positive, levels with $j = l + \frac{1}{2}$ are slightly raised and those with $j = l - \frac{1}{2}$ are slightly lowered relative to the central force energy level E_n . To complete our calculation we must evaluate a , but since this calculation is beyond the level of this book, we shall limit ourselves to producing the final result, which is

$$a = \frac{|E_n|Z^2\alpha^2}{\hbar^2 n l(l+1)(l+\frac{1}{2})},$$

where α is the fine structure constant, introduced in Example 3.6, and $|E_n|$ is the absolute value of the energy of the electron in the absence of spin-orbit interaction.

The separation between the two energy levels is

$$\Delta E_{SL} = \frac{1}{2}a\hbar^2(2l+1) = \frac{|E_n|Z^2\alpha^2}{n l(l+1)} \approx 5.32 \times 10^{-5} \frac{|E_n|Z^2}{n l(l+1)}.$$

Thus the separation between the levels due to the spin-orbit interaction is very small compared with $|E_n|$, and decreases as n and l increase. For example, for the 2p-state in hydrogen, ΔE_{SL} is about 4.6×10^{-5} eV. So the transition from the 2p-state to the 1s-state should consist of two lines separated in frequency by an amount 1.11×10^{10} Hz or a wavelength difference of about 5.3×10^{-13} m. These values should be compared with the frequency 2.47×10^{15} Hz and the wavelength 1.21×10^{-7} m corresponding to the transition in the absence of the spin-orbit interaction.

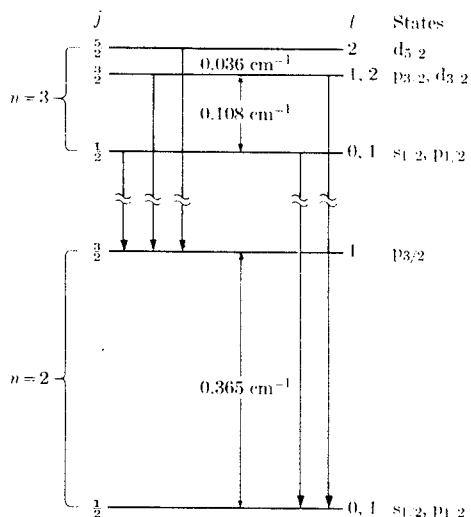


Fig. 3-23. Fine structure of the $n=3 \rightarrow n=2$ transition in hydrogen.

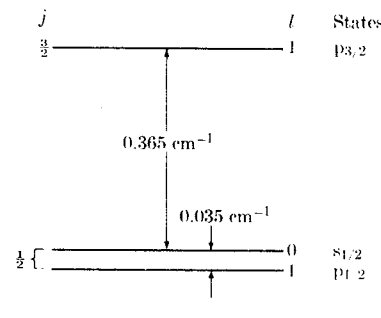


Fig. 3-24. Splitting of the $n=2$ level in hydrogen, including the Lamb shift.

When the relativistic correction given by Eq. (3.26) is added to the spin-orbit interaction, the energy levels are given, up to the first-order approximation, by the expression

$$E = E_n + \frac{|E_n|Z^2\alpha^2}{n} \left(\frac{3}{4n} - \frac{1}{j + \frac{1}{2}} \right),$$

and thus levels with the same n and j coincide. Level $n=1$ has $j = \frac{1}{2}$ only and remains single. Energy levels for $n=2$ and $n=3$ and the allowed transitions among these levels are shown in Fig. 3-23 for hydrogen. More careful measurements and more precise calculations show that states with different l but the same j do not coincide, but in fact are slightly separated. For example, the actual level arrangement for $n=2$ is as shown in Fig. 3-24 for hydrogen. The separation between the $s_{1/2}$ and the $p_{1/2}$ levels is called the *Lamb shift*.

EXAMPLE 3.8. Calculation of the magnetic moment of an electron in the presence of spin-orbit interaction.

Solution: The spin-orbit interaction $E_{SL} = a\mathbf{S} \cdot \mathbf{L}$ depends on the relative orientation of \mathbf{S} and \mathbf{L} ; that is, on the angle formed by these two angular momenta. But when the potential energy depends on an angle, a torque is applied in a direction perpendicular to the angle. Thus a torque exists perpendicular to \mathbf{S} and \mathbf{L} which makes these vectors precess. However, if no external torques are applied, the total angular momentum $\mathbf{J} = \mathbf{L} + \mathbf{S}$ must be constant. So we may visualize the effect of the spin-orbit interaction as producing a precession of \mathbf{S} and \mathbf{L} around their resultant, as indicated in Fig. 3-25.

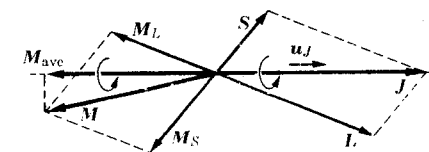


Fig. 3-25. Resultant average magnetic moment.

The magnetic dipole moment of the electron, with $g_S \approx 2$, is given in Eq. (3.33) by

$$\mathbf{M} = -(e/2m_e)(\mathbf{L} + 2\mathbf{S}) = -(e/2m_e)(\mathbf{J} + \mathbf{S})$$

and is not directly opposed to \mathbf{J} . Therefore \mathbf{M} is also precessing around \mathbf{J} . The average value of \mathbf{M} is equal to the component of \mathbf{M} parallel to \mathbf{J} . So we may write

$$\mathbf{M}_{\text{ave}} = (\mathbf{M} \cdot \mathbf{u}_J)\mathbf{u}_J,$$

where \mathbf{u}_J is the unit vector in the direction of \mathbf{J} , which may be written as $\mathbf{u}_J = \mathbf{J}/J$. Therefore

$$\mathbf{M}_{\text{ave}} = -(e/2m_e)(\mathbf{J} + \mathbf{S}) \cdot \mathbf{J} \mathbf{J}/J^2 = -(e/2m_e)(1 + \mathbf{S} \cdot \mathbf{J}/J^2)\mathbf{J}.$$

Since $\mathbf{J} = \mathbf{L} + \mathbf{S}$, we may write $\mathbf{S} \cdot \mathbf{J} = \frac{1}{2}(J^2 + S^2 - L^2)$. Thus, when we replace the squares of the angular momenta by their quantal expressions, we finally have

$$\mathbf{M}_{\text{ave}} = -(e/2m_e)g\mathbf{J},$$

where

$$g = 1 + \frac{\mathbf{S} \cdot \mathbf{J}}{J^2} = 1 + \frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)} \quad (3.40)$$

is called the *Landé factor*. Its values for spin up and spin down are

$$g = 1 \pm \frac{1}{2l+1}, \quad j = l \pm \frac{1}{2}. \quad (3.41)$$

In the presence of a weak magnetic field which does not appreciably disturb the dynamical relations of Fig. 3-25, the interaction energy is

$$E_B = -\mathbf{M}_{\text{ave}} \cdot \mathbf{B} = (e/2m_e)gB J_z = \mu_B g B m. \quad (3.42)$$

This results in more complicated Zeeman patterns than those considered in Section 3.6. The Zeeman effect, as given by Eq. (3.42), is very important because it allows us to find g experimentally and from it verify the values of j and l for the electron's state. The results of Section 3.6 are still valid when the magnetic field is strong, so that the magnetic interaction is much larger than the spin-orbit interaction and the latter can be ignored.